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June 1936

COLLOID CHEMISTRY OF CELLULOSIC MATERIALS

By

ALFRED J. STAMM
Senior Chemist, Forest Products Laboratory
Division of Research, Forest Service

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COLLOID CHEMISTRY OF CELLULOSIC MATERIALS

By Alfred J. Stamm, *Senior Chemist, Forest Products Laboratory,*[1]
Division of Research, Forest Service

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INTRODUCTION

Cellulose is supreme among all organic industrial raw materials. It not only excels in abundance and in the great diversity of its sources, but also in the range of its uses. It is the basic constituent of all plant life. It is produced in a relatively pure form, free from incrusting impurities other than the protein cuticle, in cotton and in the most abundant form as the chief constituent of wood. Its principal uses, with the exception of its use as a fuel, are all dependent upon its fibrous structural properties. These are all in the ultimate analysis colloid properties. Colloid science deals with the chemistry and the physics of surfaces, the cohesion of the ultimate structural units, and their adhesion for other materials, resulting in adsorption, surface electrical phenomena, swelling, and the like. The extent and importance of the internal surface properties can perhaps be best appreciated when it is realized that the internal surface of 1 g of cellulose is between 1 and 10 million cm^2. Although a complete understanding of the mechanism of the cohesive and adhesive forces operative over this enormous surface is at the present time lacking, recent colloid researches have gone far in the elucidation of these phenomena. Our present knowledge of the surface chemistry and physics of cellulosic materials has been invaluable in the recent phenomenal development of new cellulose products and in the improvement and profitable commercialization of older products. Further researches on cellulosic materials will undoubtedly yield greater returns than in the past.

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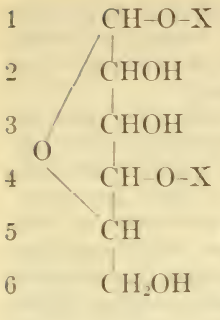
[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

This one branch of colloid science has grown at such a phenomenal rate during the first part of this century that the Forest Products Laboratory has felt the need for an up-to-date review of the subject. The purpose of this publication is to make available under one cover a connected review of the colloid chemistry of cellulosic materials in the effort to stimulate further researches and discovery, seeking always a clearer knowledge of the materials and their chemical and physical relationships.

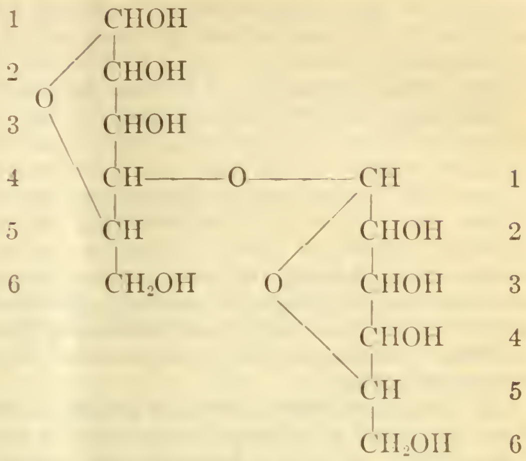
Because of the vast scope of the subject this review is confined to the studies of natural cellulosic materials and to the cellulose isolated therefrom. Cellulose derivatives will be briefly considered only in cases where corresponding data on cellulose are lacking and where the information gained therefrom is of value in interpolating properties of cellulose itself.

CHEMICAL STRUCTURE

Cellulose belongs to the carbohydrate family of compounds, being made up of carbon, hydrogen, and oxygen with the hydrogen and oxygen present in the proportions of water. Its empirical formula is $C_6H_{10}O_5$. It can be hydrolyzed almost completely to glucose, showing that it is made up of anhydroglucose units. Each unit contains three free hydroxyl groups, the positions of which have been established by the formation of 2, 3, 6-trimethylglucose. The hydroxyl groups on the 2 and 3 carbon atoms are secondary hydroxyls while that on the no. 6 carbon atom is a primary hydroxyl. Acetolysis of cellulose gives from 35 to 60 percent of cellobiose, indicating that the glucose units are united wholly or in a large part by cellobiose linkages. The structural glucose units contain amylene oxide rings; that is, carbon atoms 1 and 5 are joined together by an oxygen bridge. The linkage between the structural glucose units is through carbon atoms 1 and 4. The generally accepted structural formulae for cellulose per unit group and for cellobiose are:



Cellulose per unit group



Cellobiose

The X in the formulae represents additional anhydroglucose units. Cellulose is thus made up of long chains of glucose units the magnitude of which will be considered under the heading of Degree of Dispersion (p. 28).

The development of the structural organic chemistry of cellulose, which is beyond the scope of this bulletin, has been recently reviewed by Haworth (*82*).[2] The reader is referred to this more complete survey for further details regarding the chemical structure of cellulose.

Wood, as well as the purer forms of cellulose, is considered in this review because it lends itself more readily to the measurement of certain colloidal properties than does pure cellulose. Wood contains about 60 percent of cellulosic material, 28 percent of lignin, and minor quantities of other materials. Most of the lignin, which is the cementing material between the cellulose fibers, is in the middle lamella. A smaller quantity of lignin exists in the cell wall where it is held by either a chemical or physical union with the cellulose (*68*, *75*, *190*). Although the lignin and other noncellulosic materials have an effect upon the physical and collodial properties of the wood, these properties for wood are sufficiently similar to those for pure cellulose to justify their simultaneous consideration.

MICELLAR THEORY

The botanist Nägeli (*161*) as far back as 1858 conceived the idea of a fine organized structure for natural fibrous materials from his studies of double refraction, swelling, and mechanical properties. He concluded that these materials are built up of submicroscopic, water-insoluble, birefrigent crystallites which he called micelles. The anisotropic optical and mechanical properties he considered due to regular orientation of the micelles. Imbibed liquids he believed entered the intermicellar spaces, separated the micelles, and reduced the cohesion of the swollen body. He also believed that micelles rather than molecules are the ultimate dispersion units which on the formation of a gel unite to form a ramifying jelly structure. Nägeli's picture of the submicroscopic building units of fibrous materials received little attention at the time, but it is now recognized as the fundamental groundwork upon which most of the present conceptions of the colloid chemistry of fibrous materials are built.

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[2] Italic numbers in parentheses refer to Literature Cited, p. 66.

Although modern investigators of the fine structure of fibrous materials in general agree that these materials are made up of long, primary valence chains that exhibit the properties of Nägeli's micelles, there is still considerable diversity of opinion as to their grouping. Meyer and Mark (*152*) believe that the micelles are more or less definite bundles of primary valence chains between which swelling takes place; Astbury (*7*) and Neale (*164*) believe that the micelles are chance groupings of similarly oriented primary valence chain units with part of the chains extending from one group to another; whereas Staudinger (*236*) believes that the micelles are single-chain macromolecules.

At the present time there is a tendency, especially among investigators of crystal structure, to replace the word "micel" by the word "crystallite" so as to designate the crystalline nature of this submicroscopic structural unit. In general, however, the two words are used interchangeably.

OPTICAL PROPERTIES

DOUBLE REFRACTION

Double-refraction investigations have yielded considerable information regarding the fine structure of cellulosic fibers. Their full value was not appreciated, however, until the prediction of the anisotropic crystalline structure of fibers based on double-refraction studies was confirmed by X-ray diffraction measurements. This is in large part due to the complexity of fiber optics. The double refraction of a macrocrystal is due to the different atomic spacings in the different structural directions of the crystal lattice allowing light to pass with different velocities. Crystals belonging to the tetragonal and hexagonal systems (uniaxial crystals) possess two different indices while crystals belonging to the orthorhombic, monoclinic, and triclinic systems (biaxial crystals) have three different indices. In the case of cellulose a single crystallite cannot be observed. The optical effects are therefore composite. Although X-ray diffraction measurements have shown that cellulose belongs to the monoclinic system, the fact that orientation in a single fiber occurs only in the structural chain direction makes it impossible to distinguish more than two refractive indices. The difference between the axial and the transverse refractions is taken as a measure of the double refraction although the orientation of the structural units may not always be truly axial or transverse.

The double refraction of cellulosic materials has been shown by Ambronn (*3, 4*), who made the first intensive studies of the phenomenon, to be made up of a combination of three different double refractions, any one or all of which may be effective in a given case. The molecular or internal double refraction is similar to that exhibited by macrocrystals and is due to an anisotropic arrangement of atoms within the molecule. The second type, or particle double refraction, is due to the anisotropic arrangement of structural units, the dimensions of which are less than the wave length of light. The third type of double refraction, stress double refraction, is a special form of particle double refraction which is exhibited only when the material is under a stress. The differentiation of the first two types of double refraction, based upon Wiener's relationship (*274*), which is derived from considerations of the electromagnetic theory of light, gives the refraction of a system of rods or fibers in terms of the refraction of the components.

$$n_\gamma^2 - n_\alpha^2 = \frac{\delta_1\delta_2(n_1^2 - n_2^2)^2}{\delta_1 n_2^2 + \delta_2 n_1^2 + n_2^2} \tag{1}$$

in which n_γ is the axial refraction; n_σ, the transverse refraction of the system; and n_1 and n_2, the refractive indices of the components present in the relative volumes δ_1 and δ_2. When $n_1 = n_2$ the double refraction has a minimum or zero value and represents the molecular double refraction. The difference between this value and that existing in media of different refractive indices is due to the particle double refraction. If this particle refraction changes under tension, the portion that changes is due to a stress double refraction. Ambronn (*3*, *4*) has shown from measurements of the double refraction by the method of disappearance of the fiber in a liquid of equal refractive index, and from measurements of the interference or polarization colors in media of different refractive index, that the double refraction of denitrated cellulose nitrate fibers is made up of a particle double refraction which is always positive and a positive molecular refraction. Möhring (*154*) has shown that ramie fibers exhibit a large positive molecular double refraction together with a particle double refraction. Wächtler (*269*) has also studied the effect of applied stress on the double refraction of cellulose nitrate films. The combined double refraction increases at first with increasing stretching and then decreases asymptotically.

Frey (*69*) has shown that the double refraction of cellulose fibers determined by the disappearance of the fiber in a liquid of equal refractive index in the directions parallel and perpendicular to the fiber axis is higher the more nearly the micelles are oriented in the fiber direction. He obtained 1.595 and 1.534 for the axial and transverse refractions and 0.061 for the double refraction, $n_\gamma - n_\alpha$ of ramie, which has the most perfect axial orientation of any known natural fibrous material. Preston (*184*) obtained similar values for ramie, namely, 1.596, 1.528, and 0.068, respectively. All other cellulosic fibers with a very high degree of micellar orientation also have similar refractions and double refractions (p. 84). This is a strong indication of the identity of the various forms of cellulose. Cotton and other forms of cellulose with less perfect orientation of the structural units in general give lower axial refractions and higher transverse refractions, resulting in lower double refractions. The axial and transverse refractions and the double refraction of cotton are, according to Frey, 1.580, 1.534, and 0.046, and according to Preston, 1.578, 1.532, and 0.046, respectively. Assuming the angle of the eliptical wrapping of the fibril structure about the fiber axis of cotton to be 30°, Frey calculated the axial refraction for perfect axial alignment to be 1.596, which is practically the same as the axial refraction of ramie. Conversely, Preston calculated the angle of orientation from both the axial and the transverse refractions of cotton. The former gave a value of 30°, checking that of Frey, and the latter gave only 14.2°.

The experimentally measured value of 24° given by Balls (*9*) is, however, in good agreement with the average of these values. In order to obtain the same value for the variations in both of the refractive indices from the corresponding values for ramie, the increase in transverse refraction should be similar to the decrease in axial refraction. Preston (*184*) has shown that the axial refraction for imperfectly oriented fibers is less than the corresponding value for ramie by a greater amount than the transverse refraction of the imperfectly oriented fibers is greater than that for ramie. In fact, some chemically treated or prepared fibers, such as mercerized cotton and regenerated rayons, which show highly imperfect orientation of the structural units have lower transverse refractions than ramie. Cox points out in the discussion of Preston's paper (*184, pp. 71–77*) that mechanical and chemical treatments of fibers may partially break down the degree of association between the molecular chains in the micelles, thus tending to decrease both the observed values of axial and transverse refraction. This effect, superimposed upon the orientation effect, would tend to correct the above discrepancy.

Preston (*184*), using the value for ramie, calculated from the deviations of the axial refractions the angle of inclination of the micelles and the fiber extensibility for Lilienfeld viscose rayon, cuprammonium rayon, and ordinary viscose rayon. The angles of inclination and extensibility increase in the order given. He also showed that mercerizing of fibers under tension results in a smaller decrease in the double refraction than when the fibers are mercerized without tension. From the calculated angles of inclination of fibers mercerized under tension and without tension, he calculated the contraction occurring when no tension is applied. These values compare favorably with the observed contractions (p. 84).

Kanamaru (*107*) has studied the effect upon the resulting double refraction of removing incrusting noncellulosic materials from cellulosic fibers. He determined the double refraction of a number of different fibers after extraction with alcohol and ether, after water extraction, after dilute alkali extraction, and after chlorination and extraction with sodium sulphite. The axial refraction tends to increase and the transverse refraction decrease for the different extractions in the order given. The double refractions thus tend to increase in the order given. From theoretical considerations, using a linear mixture formula, Kanamaru calculates that the double refraction of pure ramie fibers should be 0.0758, a value about 10 percent greater than the observed value of Preston (*184*). Kanamaru (*108*) has also determined the effects of oxidation and hydrolysis upon the double refraction. When plotted against the copper number, the double refraction for both oxycellulose and hydrocellulose increase with an increase in copper number up to a maximum and then decrease again.

Signer (*210*) has studied the streaming double refraction of cellulose-derivative solutions. The solution is placed between concentric cylinders, one of which is rotated at a high speed. A beam of light is passed through the thin layer of solution between the cylinders in a direction parallel to the axis of the cylinder and its optical properties observed. The rotation of the cylinder causes an orientation of the structural units of the cellulose derivative in solution, resulting in a double refraction. Over a considerable speed range the double refraction is directly proportional to the shear which causes orientation. This demonstrates very nicely the rod-shaped nature of the structural units in solution.

X-RAY CRYSTAL STRUCTURE

Nishikawa and Ono (*168*) in 1913 obtained the first X-ray evidence of the crystal structure of cellulose from measurements on hemp. Since that time a number of investigators, notably Herzog and his coworkers (*87*, *88*), Polanyi (*182*), Sponsler and Dore (*214*) and Mark and Meyer (*145*, *147*, *151*, *152*), have contributed much information on the crystalline nature of cellulose. Cellulose from all sources has been shown to consist of definitely arranged crystallites. Measurements on ramie cellulose, in which the most parallel arrangement of micelles exists, give diffraction patterns approaching the Laue type from which a unit cell of dimensions $a=8.3$ A, $b=10.3$ A, $c=7.9$ A, and $\beta=84$ has been deduced. Each unit cell is monoclinic in structure and contains four glucose units. At first this X-ray evidence was looked at a little askance as the unit cells were interpreted to represent molecules and all other evidence pointed to much larger molecules. Diffraction intensities and chemical evidence, however, soon showed that the glucose residues in the form of amylene oxide rings are arranged parallel to the *b* dimension of the unit cell with one cellobiose group on each edge and one through the center. These form long primary valence chains arranged parallel to the fiber axis and held together laterally by secondary valences. The glucose units in the primary valence chains are arranged spirally about the longitudinal axis in such a way that a half turn in the screw axis occurs for each unit cell height. It is this periodicity that is responsible for the observed submolecular unit.

True Laue patterns are never obtained because a cellulose fiber is not a single crystal but a bundle of crystallites. The more the crystallites in a bundle deviate from axial orientation the more the pattern is shifted from the Laue type to the Debye-Scherrer ring type. It is thus possible to determine the extent of orientation from the X-ray diagrams, which vary from the most perfect orientation in ramie fibers to complete lack of orientation in precipitated films. In cotton and wood cellulose the crystallite chains are spirally wrapped and thus show only a partial orientation (*40*). The application of tension to unoriented cellulose threads and films causes the crystallites to orient (*255*).

Quantitative measurements of the orientation of the crystallites in cellulose fibers have been made by Sisson and Clark (*213*) on the basis of the distribution of the crystallites around the pencil of X-rays being proportional to the distribution of intensity around the (002) diffraction ring. Orientations varying from the most complete in the case of ramie cellulose to the most random in compression wood were obtained. The effects of mercerization and the application of tension on increasing the orientation of cotton fibers were also determined.

X-ray crystal lattice diagrams obtained from cellulose in the presence of degradation products, resins, and even lignin, are identical to those obtained on the isolated cellulose, thus indicating that these materials have no effect upon the crystal lattice and hence must be amorphous in character (*40*).

X-ray measurements have been of assistance in following the development of the cell wall of cellulose fibers. Clark (*40*) has followed this development for cotton and Ritter and Stillwell (*191*) for wood fibers. In both cases the diameter of the diffraction rings and the extent of orientation increase with time. With cotton cellulose random orientation continues up to about the thirty-fifth day at which time there is definite evidence of preferred orientation. In about 50 days the pattern indicated the maximum degree of preferred orientation. With wood cellulose the fully developed X-ray diagram is obtained in about 10 days.

X-ray measurements have also given evidence as to the size of the micelles in the solid crystal lattice. In the colloidal range the smaller the particles and the fewer the diffracting parallel planes, the less perfect is the sharply unidirectional interference of secondary waves and the broader is the diffraction maxima that characterize a given crystalline structure. Scherrer (*85, pp. 159–163*) has derived an equation giving the dimensions of the diffracting particle in terms of the breadth of the diffraction bands. Herzog (*85*) first applied this relationship to the calculation of the dimensions of the cellulose crystallites. Later Hengstenberg and Mark (*84*), using a more accurate equation of Von Laue (*131*) on measurements made with ramie fibers, obtained 500A for the minimum length and 50A for the cross-sectional dimensions, indicating that the micelle is made up of chains at least 100 glucose units long with about 60 chains in a bundle. A recent attempt by Clark (*40*) to determine these dimensions directly by means of a magnesium target instead of copper, thus increasing the X-ray wave length and, consequently, the magnitudes that can be resolved therefrom, gave results for the cross-sectional dimensions of the crystallites similar to those obtained by Hengstenberg and Mark (*84*).

Astbury (*7*) contends that discrete micellae structural units are inadequate to explain the mechanical properties of fibrous materials. He believes that the X-ray evidence just given and the double refraction phenomenon can be equally well explained on the basis of zones of preferred orientation of more or less continuous amylene oxide chains occurring throughout the structure with zones of less perfect orientation interspersed. Part of the chains making up a single oriented zone will extend through to a second preferred orientation zone and others to a third or fourth adjacent oriented zone. Astbury points out that similar coexistence of perfection and imperfection has been postulated to explain certain crystal phenomena. He further states (*7, pp. 204–205*) that X-ray evidence indicates—

> that the term "miscelle size", as used in discussions of swelling phenomena * * * has no precise meaning, but rather is a function of both the swelling agent and previous swelling history. With an "inactive" liquid, such as benzene, the "miscelle size" is limited only by the grosser imperfections of structure, while in the case of swelling by aqueous alkalis the miscelle may be synonymous with even a single molecular chain.

Neale (*164*) has expressed similar views.

Katz and his associates (*92, 112, 113, 116*) have studied the effect of swelling agents on the X-ray crystal lattice of cellulose. Swelling in water has no effect upon the crystal lattice. Swelling is therefore between the structural units rather than within the units, that is, intermicellar rather than intramicellar. There is, however, a slight tendency towards decreased orientation. Clark (*40*) has shown that the swelling of wood in water is also intermicellar. When cellulose is swollen in alkalies a change in the X-ray lattice takes place above a minimum concentration. For sodium hydroxide the changed lattice begins to appear at a concentration of about 10 percent. At higher concentrations the original lattice diagram disappears entirely and a new diagram is visible. When the alkali is washed out the original diagram returns and becomes superimposed on the retained new diagram. In concentrated nitric acid a similar change in the X-ray diagram occurs. The action of other acids in causing a changed lattice has not yet been definitely proved. Treatment with cuprammonium solution yields a changed lattice that persists on washing out the solution. Earlier measurements indicate that concentrated salt solutions have no effect upon the lattice but recently Katz and Derksen (*115*) have found a definite change with lithium thiocyanate. A changed lattice appears with 3 LiCNS to 1 H_2O and another change with 4.2 LiCNS to 1 H_2O. After washing out the salt the new diagrams persist together with the original diagram. Katz and Dreksen believe a similar effect will be obtained with other salt solutions possessing strong swelling properties. In all these cases where an intramicellar swelling is obtained the regenerated cellulose is of the "hydrate" form as will be shown later.

Katz, in the discussion of Neale's paper (*164*), points out that, if the structural hypothesis of Astbury and Neale is true, X-ray swelling data will have to be interpreted differently. If the X-ray diagram of a fibrous material remains unchanged during swelling, it can merely be concluded that "the many little islands, where the structure is strictly crystalline, do not change in their internal structure." In the ramified part a true solid solution may be formed.

It has recently been questioned if the powder diagrams of cellulose and similar substances originate in the crystal structure of these substances. Kolkmeijer and his coworker (*121*) believe that the diffraction bands are those of a hydration film surrounding the particles because the diagram is the same as that of ordinary ice. It will be shown later that thermodynamic considerations also indicate that the hydration film has an orientation similar to that existing in ice (p. 62).

OTHER OPTICAL PROPERTIES

Cellulose solutions rotate the plane of polarized light. This property appears to be due to the formation of degradation products resulting from the solution process rather than to cellulose itself. As will be shown later (p. 25) there are no purely physical solvents for cellulose. Even in cuprammonium solvent cellulose rotates the plane of polarized light. Hess and his coworkers (*91*, *92*, *93*) attribute this to a supposed definite cuprammonium-cellulose complex (p. 26). Whether this rotation should be interpreted on the chemical basis or on a purely physical basis is, however, still uncertain. Murray, Staud, and Gray (*160*) have studied the optical rotation of degraded cotton cellulose. Hydrocelluloses prepared with phosphoric, sulphuric, and hydrochloric acids were all dextrorotatory, whereas the alkaline extracts were levorotatory. Oxycelluloses prepared by oxidation with potassium dichromate and potassium permanganate and dissolved in alkali were levorotatory. Sherrard and Froehlke (*209*) have shown that the optical rotation versus time relationships of cotton cellulose and wood cellulose from different species of wood dissolved in concentrated hydrochloric acid differ appreciably. The differences between the different cellulose preparations can be explained on the basis of differences in their chemical constitution. Part of the difference may also be due to differences in physical structure causing different rates of reaction.

Cellulose was shown to be fluorescent in ultraviolet light by Hartley (*79*) in 1893. Judd Lewis (*133*) has studied this phenomenon extensively and has devised a method of photographing the fluorescent spectrum. All wave lengths below 3,300 A° are effective. "Normal" paper, filter paper, viscose, and cellulose acetate showed strong fluorescence. There is conflicting evidence as to the effect of the physical form of the material. The most recent evidence of McNally and Vanselow (*142*) indicates that the micellar orientation as well as the chemical composition affects the fluorescence.

Herzog, Kratky, and Petertil (*89*) have shown that the angle of depolarization of Tyndall light by cellulose-derivative solutions as well as solutions of other high molecular weight materials of fairly uniform dispersion changes on standing after being shaken. They have called this change in the angle of depolarization the shaking effect. It increases with an increase in concentration up to a maximum value. The maxima occur at lower concentrations for materials of higher molecular weight. Shaking effects as high as 12.5° have been obtained with acetyl cellulose. Further work will have to be done before the results can be interpreted in terms of structure.

MICROSTRUCTURE

Noteworthy microscopical observations regarding the structure and origin of plant fibers date back about 100 years (*62*, *190*). Valentin (*266*) in 1837 observed a granular structure in the cytoplasm which he believed developed into spiral lines of the cell membranes The following year Meyen (*150*) reported the existence of fibrils in the cell walls. In 1852 Agardh (*2*) separated the spiral lines and demonstrated the fibrillar nature of the structure. Stratifications in cross sections of fibers and striations on the lateral surfaces of fibers were reported in 1877 by Nägeli and Schwendener (*162*), and in 1882 by Strasburger (*244*). Wiesner (*276*) in 1886 obtained fine particles which he termed "dermatosomes" from the treatment of fibers with acids at elevated temperatures.

Recent microstructural investigations have been directed more to the isolation of the structural units. Structure within a mature intact cell wall can only be superficially observed. If, however, the fiber is subjected to mild solvent or swelling treatment, the structural units can be loosened one from another and thus made visible. Ritter (*189*, *190*) has successfully isolated a number of structural units from wood fibers. First there are the sleevelike layers which he has succeeded in slipping one from another by alternate swelling and shrinking treatments on short fiber sections. Each of these layers or sleeves can be further separated by continued treatment. At first striations along the fiber surfaces appear which later separate into fine cellulose strands known as fibrils. In the inner layers the parallel arranged fibrils are spirally wrapped at angles of from 10° to 30° to the fiber axis. The outer layer, on the other hand, is made up of fibrils wrapped almost at right angles to the fiber axis. Lüdtke (*139*) believes that the fibrils are limited in length by transverse elements intersecting them at fairly uniform intervals. Ritter does not believe that this is the case. He has isolated fibrils and bundles of fibrils as long as 230μ.

Ritter has further shown that what Lüdtke considers cross walls are very likely points along the fiber where the outer fibril wrapping is intact with swollen zones in between where the wrapping has been broken or dissolved off. This swelling will be considered further under the heading Nature of Swelling.

Ritter has further dissected the fibrils into spindle-shaped units, termed fusiform bodies, and into still smaller units termed spherical units. Ritter does not believe that the spherical units exist as such in the structure but that they assume the spherical shape as a result of swelling. All the other structural units are double refractive whereas the spherical units are not. The spherical units have thus very likely lost their anisotropic property through the disorienting effect of swelling (p. 85).

In the case of wood, hemicelluloses or even lignin may exist between the structural units of fibers. Although the major part of the lignin exists in the middle lamella (*189*, *190*), differential solvent treatments show that on dissolving the cellulose of the cell wall either a fragile porous network of lignin (*68*, *75*) or an amorphous lignin powder which probably resulted from breaking down of the porous network remains.

Lüdtke (*139*) believes that each of the structural units of all fibrous materials is enveloped in a continuous skin substance which acts as a nonswelling semipermeable membrane. This postulate was made to account for the longitudinal shortening of fibers which accompanies an appreciable transverse swelling. The swelling phenomena can, however, be explained on the basis of the different orientations of the micelles with respect to the fiber axis, occurring in the different structural units (p. 56). It thus seems highly improbable that such a hypothetical continuous skin substance exists. Of course, this does not mean that incrusting materials between structural units are not present.

Seifriz (*202*) and Thiessen (*250*) have observed fine striations along the length of cell walls of various fibrous materials with the use of a Spierer lens. The former believes these to be supermicelles and the latter believes them to be micelles. The phenomenon has since been shown by Clifford and Cameron (*43*) to result from diffraction. These diffraction lines may have some structural significance but their spacing can hardly be a measure of the dimensions of structural units.

Farr and Eckerson (*62*) have recently shown in their study of the development of the cotton fibers that from the time of the first slight bulging of the outer wall of the epidermal cell, in the direction of fiber elongation, there are in the cytoplasms particles of uniform size that appear in beadlike strands. These particles are ellipsoidal in shape, having a length of about 1.5 μ and a short diameter of about 1 μ. Their size is considerably larger than Ritter's spherical units. Farr and Eckerson's particles are, however, doubly refractive, the axial refraction being 1.565, the transverse refraction 1.530, and the double refraction 0.035. The double refraction of the particles is less than that of cellulose fibers (p. 84). The amylene oxide chains of cellulose are perhaps less oriented in the particles than in the intact fiber which may be due to a greater extent of swelling in the former than in the latter. The particles give a positive sulphuric acid-iodine color test for cellulose. They are covered with a thin layer of pectic substance which is nondoubly refractive and dissolves in dilute alkali solutions. These particles in chain formation appear to form a single fibril in the cell wall. They can be separated from the mature cotton fiber. If the dehydration of the fibers has been appreciable, mild pectin solvents are necessary to make the separation. If, however, the dehydration has been slight, the separation can be made without the use of pectic solvents. Farr and Eckerson (*63*) have prepared the small ellipsoidal units on a large scale for analytical, X-ray, and molecular-weight measurements by treatment of the fibers with 37 percent hydrochloric acid for 5 days at room temperature. These particles were free from pectic substance and showed the same properties as the particles observed in the development of the fibers. X-ray crystal structure investigations by Farr and Sisson (*64*) showed that the particles give the typical Debye-Scherrer cellulose diffraction pattern of cellulose. According to Kraemer [3] the molecular weight of the cellulose making up these particles as determined by means of the ultracentrifuge is 50,000 (p. 86).

Similar particles were obtained from other cellulosic substances. Even the bacterially formed cellulose membranes of Hibbert and Barsha (*97*) show the same beadlike chain formation of particles. Farr and Eckerson (*62*) thus believe that these elliptical structural units are characteristic of all cellulosic materials and that they are fundamental biological structural units. The question arises as to whether these structural units, which are considerably larger than the postulated micelles, can account for the properties ascribed to the micelles. Offhand this seems hardly to be the case. As was shown under the heading Double Refraction, cellulose shows a particle as well as a molecular double refraction. This particle double refraction is due to an orientation of structural units having a diameter less than the wave length of light. The elliptical particles have a diameter exceeding the wave length of light. Their orientation cannot thus account for the particle double refraction. The smaller structural unit which causes the particle double refraction may be the single amylene oxide chain of cellulose or an intermediate-sized unit of associated chains.

The most difficult problem arising as a result of the discovery of these small regular structural units is to explain how they are held together in chains. Is the pectic film a sufficiently good adhesive to account for the strength properties? Do some amylene oxide chains run through from one particle to another as postulated by Astbury (7) for micelles? The answers to these questions will have to await the obtaining of further data.

CAPILLARY STRUCTURE

GENERAL FINDINGS

All cellulosic materials exhibit a capillary structure resulting either from the tubular structure of the fibers themselves, such as in wood and other plant materials, or from the interstices between the matted unoriented or only partially oriented fibers making up the structure of such synthetic materials as paper. In the case of wood there are four distinct classes of capillary structure: (1) The resin ducts of the softwoods and the pores of hardwoods that are often visible to the naked eye; (2) the fiber or tracheid cavities or lumen which can be seen under low-power magnification; (3) the pores of the pit membranes which serve as the means of communication from fiber cavity to fiber cavity, only the largest of which can be seen with a high-powered microscope; and (4) the pores in the cell walls which approach molecular dimensions in size. In the case of synthetically prepared cellulose membranes and paper, two general types of capillaries exist: (1) The interfiber spaces, and (2) the pores in the fibers themselves. In the case of membranes obtained by regenerating cellulose from solution only the finer capillary structure approaching that of natural fiber walls is effective.

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[3] KRAEMER, E. O. THE MOLECULAR WEIGHT OF CELLULOSE. Paper presented at the meeting of the Cellulose Division, Amer., Chem. Soc., New York, 1935. (Unpublished. Title in program.)

Most of the studies of the capillary structure have been made on the basis of permeability of the material to liquids or gases, that is, a comparison of the rates of flow under an arbitrarily fixed head through specimens of the material of arbitrarily fixed dimensions. These qualitative capillary investigations will be presented first. Johnston and Maass (*101*) and Sutherland, Johnston, and Maass (*247*) have studied the rate of penetration of various liquids into softwoods from the standpoint of pulping. They found the permeability of transverse heartwood sections with thicknesses greater than a fiber length to be 100 times that of radial or tangential sections of the same thickness. In sapwood sections the flow in the fiber direction was 50 times that across the fibers. This is due to the fact that the water has to traverse 50 to 100 times as many pit membrane pores or cell checks, which serve as the means of communication between fiber cavities, when the penetration is across the fibers as when in the fiber direction. Unseasoned sapwood was 200 times more permeable than unseasoned heartwood. An increase in pressure caused a slightly greater rate of penetration at higher pressures than would be expected if it were directly proportional to the pressures. This the authors believe to be due to a stretching of the pit membranes at higher pressures, resulting in an increase in the size of the openings. The use of a back pressure had no apparent effect. The rate of penetration in all cases decreased with time to a final equilibrium rate. Presoaking did not hasten the attainment of an equilibrium rate.

The capillary structure of wood has been recently studied by Buckman, Schmitz, and Gortner (*32*). They found the permeability of transverse sections of wood to water, aqueous solutions, and various organic liquids to decrease with time to a final equilibrium value. The change in permeability to water caused by the addition of electrolytes was not a function of the viscosity. This is probably due to electrokinetic effects which modify the resistance to flow. They also found the permeability of the sections to benzene to decrease with increasing moisture content, indicating that the swelling of wood decreases the size of the effective openings.

Silvio (*211*) has studied the impermeability (reciprocal of the porosity) of paper to air. The effects of thickness of the paper, fiber dimensions, nature of the stock, and processing treatments were studied. The impermeability is not a direct function of the sheet thickness as would be expected if the structure of the sheets were identical. This deviation is very likely due to a less complete orientation of the fibers in the plane of the paper for the thicker than for the thinner sheets. The permeability was not a direct function of the applied pressure either. This is undoubtedly due to turbulent effects in the irregular relatively coarse capillary structure.

Emanueli (*61*) used a modification of the flow method in studying the capillary structure of paper. Instead of determining the rate of flow of air through the capillary system under a fixed head, he determined the ratio of the pressure drops through the paper and a calibrated glass capillary connected in series, thus avoiding the necessity of thermostatic control of the temperature. Doughty, Seborg, and Baird (*50*) have developed a convenient permeability tester for paper based on the principles of Emanueli's method. With this apparatus they have determined the effects of solid fraction and thickness of the sheet on the equivalent pore radius, the radius of a single pore that would give the same flow as all of the actual pores combined (*200*). The equivalent radius decreases with an increase in solid fraction. With a low solid fraction it decreases with an increase in thickness, and with a high solid fraction it increases with an increase of thickness.

McBain and Kistler (*141*) have studied the permeability of cellophane membranes, which have a very fine capillary structure. Cellophane is permeable to water but practically impermeable to other liquids. If, however, the water in swollen cellophane is replaced by alcohol, the cellophane becomes permeable to alcohol and if the alcohol in turn is replaced by another organic liquid in which it is soluble, the membrane becomes permeable to that liquid. Replacement of one liquid by another will be considered further under the heading of Swelling (p. 58).

DIFFUSION INTO CELLULOSIC MATERIALS

Bateman, in unpublished studies at the Forest Products Laboratory of the natural penetration of acids and alkalies into wood, observed that the tangential and radial penetrations were practically identical and followed the diffusion law. The line of advance of the solutes was very straight in contrast to that obtained under pressure-permeability conditions. This is because the rate of advance in diffusion is dependent chiefly upon the cell-wall capillarity, whereas pressure permeability depends upon the effective pit-membrane capillary sizes which vary considerably from fiber cavity to fiber cavity.

Bateman and Salzburg, and Bateman and Hohf, in unpublished studies at the laboratory of the rate of drying of wood blocks confined to a single structural direction under conditions which removed the vapor as fast as it came to the surface, showed that the drying in each of the structural directions is a diffusion phenomenon. Complexities of the structure and possible combinations of both liquid and vapor flow, however, greatly complicate the problem.

Lusby and Maass (*140*) studied the capillary structure of wood by means of natural penetration of water into dry wood immersed in water and by diffusion of electrolytes into water-saturated wood. They used specimens of the same weight with a square cross section and different lengths. Measurements of the time of sinkage and time of attainment of half concentration at the center of the blocks showed that in each case there was a least effective shape. In shorter blocks the penetration was largely longitudinal and in longer blocks transverse. Natural penetration of water longitudinally was at least 10 times that transversely while the diffusion of sodium hydroxide was practically the same longitudinally and transversely and the diffusion of sodium chloride and hydrochloric acid was about 3 times as great longitudinally as transversely.

The rate of diffusion of water vapor through wood was studied by Pidgeon and Maass (*181*) by determining the time taken for samples of different thickness to come to equilibrium with a relative vapor pressure of 22 percent in an evacuated system. Continuous measurements were made by suspending the specimens from a quartz helix balance. The time to the half equilibrium moisture content increases with an increase of the thickness of transverse sections and becomes quite appreciable when the average fiber length is exceeded, especially in heartwood. Diffusion in the radial direction was still considerably slower. In thin transverse sections the vapor is readily accessible to all the wall surface where sorption takes place. In thicker sections and sections cut in the other structural directions, vapor has to pass through the fine communicating pit-membrane pores or condense on the cell walls and again vaporize on the other side after diffusing through the wall. Both of these factors will greatly increase the time of attainment of equilibrium.

Cady and Williams (*36*) have recently studied the diffusion of urea, glycerol, and lactose into wood in the longitudinal direction. From their data they calculated the effective capillary cross section after correcting for the blocking effect due to passage through the pit membranes. This correction will later be shown to be unnecessary as the fiber cavities themselves furnish practically all of the resistance to diffusion. The quotient of the diffusion into a block of wood and the diffusion into the same dimensions of water gives the effective fractional capillary cross section of the fiber cavities.

Neale and Stringfellow (*165*) in studying the absorption of dyes by cellophane found that the taking up of dye follows the diffusion law. A sheet of half the normal thickness dyed to a given fraction of saturation in one-quarter of the time required by the sheet of normal thickness.

The seat of resistance to the passage of materials through wood under diffusion conditions has been calculated by the author,[4] using capillary information (pp. 16, 20). Considering the series combination of fiber cavities and the pit-membrane pores and pores in the cell wall with the latter two in parallel, it can be shown that the seat of resistance to diffusion in the longitudinal direction in a wood-swelling medium is almost entirely in the fiber cavities, whereas in the two transverse directions it is of the same order of magnitude in the fiber cavities and in the cell-wall pores. The diffusion through the pit-membrane pores is practically negligible for all small molecules dissolved in swelling solvents in comparison with the diffusion through the cell-wall pores. In the case of diffusion of a solute in a nonswelling medium, the effectiveness of the cell-wall pores becomes zero and the resistance to diffusion is almost entirely in the pit-membrane pores. In the case of the diffusion of a vapor the condition is similar. Condensation will occur in the cell-wall capillaries at high relative vapor pressures and at low relative vapor pressures the capillarity of the cell wall will be very small, thus practically eliminating them as a source of flow.

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[4] STAMM, A. J. DIFFUSION VERSUS PRESSURE PERMEABILITY IN WOOD. Paper presented at the meeting of the Colloid Division, Amer. Chem. Soc., San Francisco, 1935. (Unpublished. Title in program.)

These calculations also give a limiting low value of 1.65 for the ratio of diffusion of a solute in a swelling medium in the longitudinal direction to that in the transverse directions. This value compares favorably with Lusby and Maass' experimental value of 3 (*140*). For diffusion in nonswelling media the calculated ratio is 5.2.

MAXIMUM CAPILLARY RADII FROM OVERCOMING OF SURFACE TENSION

Several different methods have been used for determining the actual size of the capillaries in fibrous materials. The simplest method is that of overcoming the surface tension of a liquid in the capillary system by applying just sufficient air pressure to displace the liquid. This method gives the size of the most permeable pore in the parallel combination at the point of minimum radius. If Q is the pressure that will just displace the liquid from the capillary and allow air to pass, r is the minimum radius of the capillary, and σ is the surface tension of the liquid, then

$$r=\frac{2\sigma}{Q} \tag{2}$$

Bartell and Carpenter (*14*) have determined the most effective pore radii of collodion membranes to be 0.3μ to 0.8μ. McBain and Kistler (*141*) obtained 0.02μ to 0.03μ for the pore radii of cellophane membranes. Bechhold, Schlesinger, and Silbereisen (*21*) in studying various membrane materials found that displacing isobutyl alcohol with water was more satisfactory than displacing water with air because the interfacial tension is only 1.8 dynes per centimeter as compared with 72 dynes per centimeter for the surface tension of water. In this way the required pressure is reduced to 2.5 percent of that needed to displace water with air, thus materially avoiding the stretching of the membranes and distorting of the capillaries. Bechhold (*20*) in a recent investigation obtained maximum pore radii with this method of 0.09μ to 0.25μ for various collodion membranes (p. 85).

The author (*218, 220, 226, 228, 231*) has applied the method of overcoming the surface tension to the study of the capillary structure of softwoods. The pressure required to displace water from transverse sections increases moderately with an increase in thickness of the section up to the maximum fiber length, at which point there is a sudden large increase in the required pressure followed by a slower increase. This is due to the fact that open fiber cavities constitute the effective capillary structure at first. Their effectiveness decreases with an increase in thickness due to the increased probability of inclusion of restricted points in the irregular fiber cavities and the inclusion of the tapered end portions of the fiber cavities. When the maximum fiber length is exceeded, the much smaller pit-membrane pores become effective. Increasing the thickness so that a number of these have to be traversed in series gives values approaching the average pit-membrane pore size rather than the maximum. The pit-membrane pore radii obtained in this way ranged from 0.04μ to 5.0μ for the heartwood of several species and from 0.18μ to 11μ for the sapwood (p. 85). The method further gives a measure of the maximum fiber length (0.45 to 0.56 cm for several different softwoods).

AVERAGE CAPILLARY RADII FROM PRESSURE PERMEABILITY

The approximate average size of the capillaries in a porous material can be determined from a combination of pressure-permeability measurements and capillary cross-section measurements, using Poiseuilles' equation for the flow of liquid through the capillary system under an applied hydrostatic pressure

$$V=\frac{n\pi r^4 P}{8\eta l} \tag{3}$$

in which V is the rate of flow of a liquid or vapor of viscosity η through n capillaries with an average radius r and length l under a pressure P, all expressed in centimeter-gram-second units. In this equation all of the factors are directly determinable with the exception of n and r. The value of r can be determined, however, if the effective capillary cross section $\pi r^2 n$ is known. The average capillary cross section or the effective capillary cross section under definitely specified conditions can be calculated from the moisture content of the capillary filled system or from the bulk density of the cellulosic material and the density of the solid cellulosic substance. Bjerrum and Manegold (*26*) have done this for six different cases: (1) In which all of the capillaries, assumed to be circular, extend across the membrane at right angles to the surface; (2) the circular capillaries are assumed to be uniformly distributed in the three structural directions perpendicular to each other; (3) the circular capillaries are assumed to be equally distributed in all directions. Each of these conditions for slits were also considered. Conditions (2) and (3) were shown to give identical results and 1.73 times greater than (1) for the capillary radius. The circular pores gave values 2.31 times greater than the slits. For their collodion membranes they obtained values of r for conditions (2) and (3), ranging from 0.9 mμ to 30 mμ under different conditions of preparation. Bjerrum and Manegold's calculations of the effective cross-sectional area, however, involve another assumption which they do not state; namely, that the capillaries in the three different structural directions are independent capillaries and do not intersect. For intersecting capillaries as exist in the interstices between packed spheres, the effective void volume V_f, according to Dumanski's relationship (*54*) as expressed by Cady and Williams (*36*), gives the effective void cross section

$$q=1-(1-V_f)^{2/3}=1-\left(1-\frac{\rho_w}{\rho_s}\right)^{2/3} \tag{4}$$

in which ρ_w is the bulk density of the membrane and ρ_s the density of the membrane substance. This form of capillary structure seems more logical than that assumed by Bjerrum and Manegold (*26*). The data of Bjerrum and Manegold on this latter basis give values of r 0.765 times the above values for the low fractional void volumes (0.04) and 0.610 times the above values for the high fractional void volumes (0.930). The above radii would thus be 0.69 mμ and 18.3 mμ, respectively. It is thus evident that considerable variation in the capillary sizes is obtained under different capillary distribution assumptions.

Duclaux and Errera (*52*) obtained 13 mμ as the average pore radius of cellulose acetate membranes on the assumption that all the capillaries extended across the membrane at right angles. Morton (*157*) has determined the average pore radius of viscose films after a pretreatment with various concentrations of sodium hydroxide solution, using Bjerrum and Manegold's assumption of three-dimensional distribution of the capillaries. He obtained values ranging from 1.5 mμ for the untreated films to 9.4 mμ for films treated with a 10-percent sodium hydroxide solution. Hitchcock (*99*) used a more exact method for determining the capillary cross section of membranes; namely, that of measuring the electrical conductivity of a dilute salt solution filling the void structure. The effective capillary cross section is obtained directly from the quotient of this conductivity and the bulk conductivity of solution having the same dimensions as the membrane. In these measurements the salt solution concentration has to be sufficiently great to make the surface conductivity negligible in comparison with the bulk conductivity (p. 33). No assumptions regarding capillary distribution are necessary. Hitchcock (*99*) obtained values for the average pore radii of 3 to 20 mμ for collodion membranes (p. 85).

The author has determined the average effective capillary radii in wood from a combination of the permeability of wood sections to water and electro-osmotic flow measurements of the effective capillary cross section (*218*, *220*). A differential pressure permeability apparatus similar to that of Emanueli (*61*) was used. Instead of determining the rate of flow, the pressure drops occurring through the wood section and a calibrated glass capillary connected in series were measured. With this form of apparatus the rate of flow through the two capillary systems in series are equal. The viscosities through each are also equal; hence making temperature control unnecessary. The average effective capillary radius r can thus be expressed as follows

$$r=\sqrt{\frac{\pi r_0^4 l P_0}{l_0 q P}} \tag{5}$$

in which r_0 and l_0 are the radius and length of the standard glass capillary, l is the effective length of the path through the membrane, q is the effective capillary cross section of the membrane, and P_0 and P are the pressure drops through the glass capillary and the membrane, respectively. This method of measuring permeability has the distinct advantage of affording a simple means of correcting for any turbulent effects. In the absence of turbulence the ratio $\frac{P_0}{P}$ will not change with applied pressure. In practice there is a slight linear change with applied pressure. Extrapolation of this linear relationship to a zero applied pressure gives directly the turbulent free permeability.

Transverse sections of wood of different thickness showed a rapid decrease in permeability with increasing thickness up to the maximum fiber length. Thicker sections gave but a slight decrease in permeability per unit increase of thickness. In the thinner sections the water flowed almost entirely through the open lumen of the fibers that were cut across twice. Where the sections were thicker than the fiber length the water had to flow from one fiber lumen to another through the communicating small pores in the pit membranes or pit checks which furnished practically all of the resistance to flow. The sharp break in the permeability curve thus furnishes another simple means of determining the maximum fiber length.

When the size of the pores in the pit membranes which connect fiber cavity to fiber cavity and furnish practically the entire resistance to flow through thick transverse sections (p. 15) are sought, the foregoing methods for determining the capillary cross section fail as they measure fiber cavity rather than pit-membrane pore cross sections.[5] The effective capillary cross section of the pit-membrane pores can, however, be obtained from electro-osmotic flow measurements. When these are made upon transverse wood sections of different thickness a decrease in the rate of flow occurs with an increase in thickness. This decrease is rapid until the minimum fiber length is reached beyond which it is more gradual. At the maximum fiber length the rate of flow per unit potential gradient becomes constant. This rate of flow can be converted to terms of effective cross section in a simpler and more accurate way than was previously used (*220*). The electro-osmotic flow obtained by extrapolating the flow-thickness curves to zero thickness corresponds to the flow for the average fractional fiber cavity cross section which, in turn, is equal to the fractional void volume obtained from the density (p. 15). The fractional effective pit-membrane pore cross section can then be obtained from a proportionality of the rates of flow and the cross section. Pit-membrane pore radii for several different softwoods ranging from 7 mμ to 12 mμ were obtained from the combination of pressure permeability and electro-osmotic flow measurements in this way (*220*). Incidentally the electro-osmotic flow method also furnishes a statistical method for determining minimum, approximate average, and maximum fiber lengths (*220*).

The size of the effective capillaries in wood just given are for wood in the completely swollen condition. The author (*231*) has recently determined the equilibrium permeability of wood to air of different relative vapor pressures, using a differential pressure-drop apparatus quite similar to that used for liquid flow. In this case the volumes of air passing through the wood section and the standard capillary are not equal because of the expansion. This correction is negligible for small pressure drops, but for appreciable pressure drops can be directly corrected for by multiplying the pressure-drop ratio by the ratio of the average pressures on the wood section and the standard capillary. The correction is automatically taken account of in making the aforestated correction for turbulence by extrapolating the pressure-drop ratio to zero applied pressure (p. 18). From these measurements it was shown that the pit-membrane pores increase in size on drying of the wood. The increase in the radius of the effective openings may be as much as 35 percent.

The author [6] has also been able to show from calculations involving the various capillary sizes and areas in wood that the resistance to flow under pressure permeability conditions in all the structural directions is almost entirely in the pit-membrane pores. The pressure permeability of the cell walls to liquids is negligible in comparison to that of the pit-membrane pores for all but the very most resistant woods and is zero for all woods in the case of vapor flow.

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[5] Supposed values of the ratio of the effective thickness of the pit membranes traversed in series to the thickness of the pit-membrane pore cross section traversed in parallel were obtained from electrical conductivity measurements of salt solutions filling the capillary structure (*227*). In these calculations it was assumed that the conductivity through the cell walls was negligible in comparison with the conductivity through the coarse capillary structure. This assumption has since been shown to be in error and hence the calculated values of the pit-membrane pore radii are erroneous.

[6] See footnote 4, p. 15.

DISTRIBUTION OF CAPILLARY SIZES

The distribution of size of capillaries in cellulosic membranes has been determined by Bechhold (*20*) by combining the methods of overcoming the surface tension and pressure permeability. As was shown previously, the overcoming of surface tension method gives the size of the most effective capillary. When the pressure is increased above that just required to overcome the effect of surface tension in the largest capillary in the parallel combination, two things occur. The velocity of flow through this capillary is increased and the surface tension is overcome in smaller capillaries so that they too contribute to the flow. The rate of flow through the membrane will hence increase faster than a direct proportionality to the pressure. From this increase in the rate of flow beyond proportionality to the pressure for each pressure increment the rate of change of permeability per unit change in radius can be calculated for each radius. Bechhold gives several distribution curves calculated on this basis. The membrane with the smallest pore range, 30 $m\mu$ to 90 $m\mu$, had a most probable pore radius of 55 $m\mu$.

The author (*231*) has also developed a method for determining the distribution of pore sizes applying Kelvin's equation relating the vapor pressure in equilibrium with a drop of liquid or a liquid held in a capillary system to the radius of the drop or of the capillary

$$r=\frac{2\sigma M}{\rho RT\,ln\,p_0/p} \qquad (6)$$

in which r is the radius of the capillary or of the drop, p_0 is the vapor pressure over a plane surface, p is the vapor pressure over the capillary or the drop, σ, M, and ρ are the surface tension, molecular weight, and density of the liquid, respectively, R is the gas constant and T the absolute temperature. The equilibrium permeability of wood sections to air of different relative vapor pressures was determined, using the differential pressure drop apparatus previously described (p. 18). When the square root of the pressure drop ratio was plotted against the equilibrium moisture content of the sections a linear relationship in which an increase in permeability accompanied a decrease in moisture content resulted below a moisture content in equilibrium with a relative vapor pressure of about 90 percent. At higher moisture content values the permeability decreased rapidly due to elimination of part of the capillaries as channels of flow because of condensation of water vapor in them. The capillary sizes that would just cause condensation of water vapor at each of the equilibrium vapor pressures were calculated from equation (6) and plotted against the corresponding changes in permeability. The first derivative of this curve gives the distribution curve for the rate of change of permeability per unit change in radius against the radius. Such distribution curves were obtained for transverse sections thicker than the maximum fiber length and for thin radial and tangential sections of white pine heartwood. All the sections gave a similar minimum pore radius of 10 mμ. The radial and tangential sections gave almost identical maximum and most probable radii, namely, 74 mμ and 28.5 mμ. The transverse section gave considerably higher maximum and most probable values, namely, 5 μ and 36.5 mμ, respectively. This is due to the fact that only 4 pit membranes are traversed in series in this case and over 30 in the case of the radial and tangential sections. The probability of 4 of the larger openings occurring in series in the transverse sections is, of course, much greater than the probability of 30 of the larger openings occurring in series. The latter values thus tend toward giving more nearly average values. This is also indicated by the fact that the radial and tangential sections give practically identical most probable and average values.

ULTRAFILTRATION

The effective pore sizes of membranes have also been estimated by ultrafiltration measurements. Bechhold (*20*) and Elford (*59*) have perhaps made the most extensive measurements of this type. They both find that the particles have to be somewhat smaller than the pore sizes but they are not in very good agreement with regard to how much smaller. Bechhold gives the optimum particle size-pore size ratio range as 1/15 to 1/8, whereas Elford gives 1/3 to 1. In filtering hemoglobin through collodion membranes Bechhold found the ratio to be 1/10 and Elford obtained 1/2. Morton (*157*) believes that Elford's ratio range should be shifted to 1/5 to 1/3 as Elford determined his membrane pore sizes on the assumption that the capillaries are all at right angles to the plane of the membrane. This assumption, however, was shown previously (p. 17) to be in better agreement with the Dumanski assumption (*54*) than the Bjerrum and Manegold assumption (p. 17). Elford also found that the first falling off of the filtrate concentration occurs in membranes with pores two to three times the radius of the pores in membranes which just completely prevent the passage of particles. The fact that membranes do not act as ordinary sieves is attributed to electrokinetic and adsorption effects at surface. These effects will, of course, be appreciable only in fine capillaries. They are, however, of sufficient magnitude to make the estimation of particle size of materials of colloidal dimensions or the converse estimation of the size of the pores in a membrane doubtful by this method. The method, however, will give the correct order of magnitude. Care should be taken to use particles or macromolecules with the same charge with respect to water as that of the membrane (p. 34) so as to minimize coagulation and adsorption effects.

Morton (*157*) determined the permeability of viscose membranes to various organic dyes. Membranes with average effective pore radii of 9 mμ allowed all the dyes tested to pass through to some extent. A greater proportion of the dye was filtered out with the slow dyes than with the rapid. The presence of sodium chloride increased the filterability up to an optimum value. Morton believes this to be due to a change in dispersion of the dye, but Robinson believes it due to electrokinetic effects (*157*). The author found various softwoods to be partially permeable to a mercury sol containing particles having a diameter of approximately 8 mμ.

CAPILLARITY IN SHEET DIRECTION

The capillary structure of sheets of cellulosic material in the sheet direction have been studied by determining the rate of capillary rise of liquids in strips of the material that were suspended vertically in the liquids. Lucas (*137*) has deduced a theoretical equation

$$h^2 = \frac{r\sigma t}{2\eta} \tag{7}$$

from Poiseuille's equation for capillary flow (equation 3, p. 17) and the equation for capillary rise in which h is the height of rise in time t of a liquid with surface tension σ and viscosity η that completely wets the fiber, and r is the radius of uniform straight capillaries that will give the same rise as the irregular capillary system in the fibrous material.

Measurements on filter paper strips in different liquids showed $h^{1/n}$ to be proportional to t with n varying between 0.424 and 0.50, indicating that the theoretical relationship between h and t is virtually satisfied. Simmonds (*212*) has applied the method to the study of cartridge and blotting papers. He obtained similar values of n to those found by Lucas. Calculation of the average effective pore radius gave values ranging from 0.02 to 1.0μ. The ratio of the capillary sizes in the machine direction to those across the machine direction varied from 1.1 to 1.7 for the different papers. Peek and McLean (*176*) in a recent publication have deduced the foregoing relationship in a more general form for variations in the dimensions of a capillary. On the basis of a uniform distribution of pore sizes, they obtained pore radii varying from 4.0 to 40μ in the filter paper which they used (p. 85). They verified this order of magnitude photomicrographically. The relative values of the surface tensions of a number of organic liquids obtained from the rate of capillary rise were also found to be very nearly proportional to the actual surface tension values, giving further confirmation of the accuracy of the theoretical equation.

CAPILLARITY OF THE CELL WALLS

The capillarity of a cell wall itself can be estimated from the relationship between the moisture content and relative vapor pressure, using Kelvin's equation relating the capillary radius of the pores to the relative vapor pressure in equilibrium with the water in the pores (p. 20). A distribution of capillary-size curve can be obtained by taking the first derivative of the moisture-content capillary-size curve. For wood a curve with a most probable value at 0.65 mμ and an average value at about 5 mμ is obtained.[7] The most probable value is for capillaries of the order of molecular size and hence may not have any real significance as Kelvin's equation would hardly be expected to hold for such small capillaries. Experiments show, however, that small molecules can diffuse through the cell walls (*229*). For capillaries of this size in the cell wall the Ladenburg (*129*, *130*) correction for the passage of materials through fine capillary tubes becomes quite appreciable; in fact, the correction may be considerably larger than those which he considered.

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[7] See footnote 4, p. 15.

Elöd and Schmid-Bielenberg (*60*) made the interesting observation that the velocity of acetylation of different dry fibers increases in the order of decreasing orientation of the structural units, namely, flax, hemp, ramie, and cotton. Poorer orientation means poorer packing and hence a greater chance for intermicellar spaces.

MECHANICAL PROPERTIES

Cellulose fibers are exceedingly strong in the longitudinal direction. Flax has a tensile strength of over 100 kg per mm². Well-oriented viscose fibers approach very closely to this value, while cotton varies from about one-quarter to three-quarters of this value. The strength of the flax fiber approaches that of the best steel, which has a tensile strength of about 170 kg per mm², and exceeds that of many metals (p. 85). From the work required to break the C–C, C–H, and C–O bonds, Mark (*143*) has made some interesting theoretical calculations of the fiber strength that would be expected if a fiber were made up of one continuous primary valence chain. A calculated tensile strength of 800 kg per mm² was thus obtained. The reason the actual strength values are much less than this is that these chains, although long in a molecular sense, are quite short in the macro sense and, consequently, the strength is determined by the resistance to shear of one chain upon another; that is, the resistance afforded by the secondary valence cohesion forces of hydroxyl or aldehyde groups. Mark (*143*) has also compared the breaking strength of a sugar crystal, which is 30 kg per mm², with the tensile strength of cellulose. The forces here involved are the secondary valence forces of hydroxyl and aldehyde oxygen atoms of the different molecular layers for each other, the same as in cellulose. This value is considerably less than the tensile strength of flax. The difference can be explained, however, on the basis of a greater surface of shear for the fibers which pull apart rather than break across.

The extensibility of a cellulose fiber depends upon the orientation of its component micelles (p. 6). If a fiber made up of perfectly oriented micelles is put under tension, the micelles will glide over each other, the cross section of the fiber will diminish, and the fiber will break within an extension of less than 2 percent. If, on the other hand, there is only a partial micellar orientation, applied tension will at first cause orientation, as well as extension with a subsequent increase in strength. Starting with the equation of Eckling and Kratley (*55*) connecting the extent of orientation with the amount of extension, Mark (*146*) has developed a theoretical relationship between the strength of the fiber τ, the extension ν, and the axis ratio of the micelles θ, as follows:

$$\tau = \tau_0 \frac{\nu^3}{1-\theta+\theta\nu^3} \tag{8}$$

This relationship seems to hold quite well as a first approximation.

The strength of a synthetic fibrous material such as paper is a complex function of the strength of the individual fibers, their dimensions, the extent and condition of the fiber surface, the orientation of the fibers, and the compactness of the sheet. It is thus extremely difficult to factor the effects of the different variables. Doughty (*49*) has made considerable progress in determining the effects of these variables upon the strength. His investigation indicates that the tensile strength of a sheet of paper is largely dependent upon the compactness of the sheet, that is, its solid fraction. Sheets of the same solid fraction made from slightly beaten and unbeaten stock show that a slight beating increases the tensile strength. Further beating has little effect upon the strength. Dehydration and repulping decrease the strength. The short fiber length fraction of the pulp results in a sheet of reduced tensile strength. The relationship between the strength and the solid fraction can, in general, be expressed by the equation

$$\tau = bf^{m} \tag{9}$$

in which τ is the structural tensile strength, f is the solid fraction, and b and m are constants, the b representing the strength for unit solid fraction. The values for this constant approach the tensile strength of isolated fibers but, of course, are never equal to it. The value of b also varies with the consistence of the stock from which the sheet is made. For the same solid fraction, sheets made from pulps of higher consistency show lower tensile strengths, presumably because of the poorer orientation of the fibers in the plane of the sheet. The consistence also affects the solid fraction obtainable under the same wet pressure, a high consistence giving a large solid fraction. The relationship between the strength for unit solid fraction b and the consistence of the stock Z can be expressed by the equation

$$b = kZ^{-m'} \tag{10}$$

in which k and m' are constants. The constant k represents the strength for unit consistence corresponding to the condition of complete disorientation. The combined equation

$$\tau = kf^{m-}Z^{m'} \tag{11}$$

gives a reasonably good representation of the effect of part of the sheet variables on strength.

The strength of a swollen fiber, in general, increases upon drying. This is explained on the basis of the secondary valence forces between micelles, which in the swollen condition are partially satisfied by mobile water, being brought closer together on drying and thus satisfying each other. This phenomenon is well illustrated in wood. Practically no change in strength occurs on drying until the fiber-saturation point, which is the moisture content below which the activity of the water is less than unity, that is the moisture content below which none of the water exhibits the properties of free water, is reached. Below the fiber-saturation point the strength increases almost linearly with a further decrease in moisture content (*251*, *279*). In certain twisted fibers the wet strength is greater than the dry strength. This appears to be caused by a drawing together of the micelles on swelling, resulting in the fibers tending to coil still tighter. Lüdke (*138*) has studied the tensile strength of regenerated cellulose in different liquids. In such dry, nonpolar, nonswelling liquids, as benzene, the tensile strength is the same as it is in air. Liquids, such as water, glycerine, and formamide, that cause swelling result in a considerable decrease in tensile strength of the fibers. Such liquids as dry ether and alcohol, which have a tendency to remove water from the fibers, cause an increase in the strength of water-swollen fibers.

Ridge and Bowden (*188*) have shown that the degradation of cotton and various viscose and cuprammonium rayon yarns with hypochlorite solutions causes a decrease in strength which is accompanied by an increase in the fluidity of the cellulose in cuprammonium solutions. A practically linear relationship exists between the decrease in strength and the increase in fluidity. The decrease in strength per unit increase in fluidity is further practically constant.

DISPERSION MEDIA

Cellulose is unique among colloidal materials in that it can be dispersed in only a relatively few aqueous media, practically all of which are concentrated solutions. It is questionable if cellulose in any of these media ever exists in the native form. Cellulose regenerated from its solutions, according to the classification of Sheppard (*203*) can be either in the "hydrate cellulose" or "hydro-oxycellulose" forms. The hydrate cellulose, as was shown under the heading of X-ray crystal structure, has an expanded crystal lattice and also an increased sorptive power which will be discussed later. The hydro-oxycellulose does not give an altered crystal lattice, the change being more of a chemical nature; that is, a surface hydrolysis or oxidation. The hydrate cellulose precipitated from dispersion media may, of course, have undergone "hydro-oxy" changes as well.

CUPRAMMONIUM SOLVENT

One of the oldest and most important discoveries of cellulose chemistry, which would now be considered as colloidal, is the practically simultaneous discovery by Schweizer (*199*) and Mercer, reported by Parnell (*171*), of the solvent power of cuprammonium solution for cellulose.

This dispersion media, which is an ammoniacal solution of cupric hydroxide, has been prepared by two general methods. Specially prepared cupric hydroxide is dissolved in ammonia (*48*), or air is bubbled through copper turnings in strong ammonia (*103*). The solvent itself has been shown to be colloidal in nature, small amounts of cupric oxide or hydroxide being colloidally dispersed in the cuprammonia complex (*25*, *225*).

The higher the concentration of copper in the cuprammonium solution the greater is its solvent power for cellulose. Because of this solvent variable an effort has been made to standardize the solvent concentration for viscosity measurements. The tentative concentration recommended by the committee on the viscosity of cellulose (*39*) is 30 ± 2 g of copper, 165 ± 2 g of ammonia, and 10 g of sucrose per liter. The solvent power also varies considerably with the condition of the cellulose. Native cellulose can be dissolved to the extent of 4.5 percent in the concentrated solvent (*175*). When the cellulose has been mercerized or slightly oxidized with a carefully regulated treatment with calcium hypochlorite, concentrations as high as 10 percent can be obtained. It is these latter concentrated solutions that are used in the cuprammonia process for manufacturing artificial silk. A complete description of this process is given by Avram (*8, pp. 320–338*).

Hess and Trogus (*94*) have extensively studied the swelling and solution of cellulose in alkaline solutions of cuprammonium solvent. For any given cuprammonium solution concentration the solubility of cellulose increases with increasing alkali concentration up to a maximum and then decreases. The maxima are higher for higher copper concentrations.

A difference of opinion still exists as to whether cellulose combines chemically with the copper ammonia complex, or if the complex is merely adsorbed. Hess (*92*, *93*) has proved, at least to his own satisfaction, by means of optical rotation that a stoichiometric combination of 1 Cu:1 $C_6H_{10}O_5$ is formed. Baur (*19*), on the other hand, analyzed Hess' data from a different point of view and obtained the characteristic adsorption curve. When the concentrations were substituted in the mass law equation no constant was found.

Dispersions of cellulose in cuprammonium solvent are quite unstable. Small amounts of oxygen have a very appreciable effect upon the viscosity. The solvent seems to have a slight oxidizing effect upon the cellulose even in relatively air-free systems (*186*). The ammonia, likewise, readily undergoes oxidation with the formation of nitrites. When, however, the greatest precautions are taken to exclude oxygen, the chemical degradation of the cellulose seems to be slight. Cuprammonium solution perhaps comes the closest to being a true physical solvent of any of the cellulose solvents. Cellulose regenerated from cuprammonium solution, however, is in the "hydrate" state.

Amines may be substituted for the ammonia in cuprammonium solvent. Traube (*254*) states that primary aliphatic diamines saturated with cupric hydroxide have a greater solvent power for cellulose than cuprammonium solution with an equal ammonia concentration. Solutions containing as little as 2 to 8 percent ethylene diamine are effective as solvents.

ACID SOLVENTS

Concentrated sulphuric, hydrochloric, and phosphoric acids act as solvents for cellulose. Due to the strong hydrolytic action, however, quantitative reprecipitation can only be brought about if the solutions are kept cool, and then only after relatively short periods of time after solution. Guignet (*74*) treated cellulose with an ice-cold 70-percent solution of sulphuric acid and obtained a clear, yellowish solution that could be reprecipitated by dilution with cold water. Willstätter and Zechmeister (*278*) dissolved 13 percent of cellulose in 40-percent hydrochloric acid in 10 seconds. Addition of water after 45 minutes caused quantitative precipitation. The author dissolved cotton linters alpha cellulose in 84-percent phosphoric acid and held the solution at 10° C. for 24 hours. The cellulose was then reprecipitated with water and filtered. The Molisch test for carbohydrates made on the concentrated filtrate showed no carbohydrate present, thus indicating that practically none of the cellulose was hydrolyzed to the extent that it could not be reprecipitated. Similar tests at higher temperatures gave a test for carbohydrates in the filtrate. Hydrofluoric and hydrobromic acids also act as temporary solvents for cellulose. All of the acids will dissolve "hydrate cellulose" and partially degraded celluloses in concentrations below which they have no solvent action on native cellulose. It is not known if reprecipitation from these acids forms "hydrate cellulose." As treatment with strong nitric acid develops the "hydrate" form of cellulose, these solvent acids may have a similar effect.

SALT SOLVENTS

Cellulose can be dispersed in hot concentrated solutions of a number of different highly soluble salts. As early as 1852 Barreswil (*13*) found that hot concentrated zinc chloride solution swells and dissolves paper. Solutions of cellulose in zinc salts have been used for producing threads and filaments, but their use has disappeared because of the degradation of the cellulose.

Dubosc (*51*) in 1905 discovered that certain thiocyanates acted as cellulose solvents in hot saturated solutions. Calcium thiocyanate is perhaps the best of these. At its boiling point, 133° C., it is reported to dissolve as much as 7 percent of cotton. Von Wiemarn (*272*, *273*) has published many papers on the dispersion of cellulose in saturated salt solutions. According to him the thiocyanate and iodide salts of calcium and strontium are among the most effective dispersing agents. Williams (*277*) has also done considerable work on the dispersion of cellulose in salt solutions. He found no case in which the cellulose was peptized below a temperature of 135°. Herzog and Beck (*86*) give the following order for the effectiveness of cations and anions in dissolving cellulose in their boiling saturated solutions:

$$\mathrm{Ca} > \mathrm{Ba}$$
$$\mathrm{Li} > \mathrm{Na} > \mathrm{K} > \mathrm{NH_4}$$
$$\mathrm{CNS} > \mathrm{I} > \mathrm{Br} > \mathrm{NO_3} > \mathrm{SO_4}$$

The latter members of both series cause swelling rather than solution even when combined with the oppositely charged ion at the head of the series. It is of interest to note that these series are practically the same as the well-known lyotropic series, the ions listed at the head of the series being the most hydrated.

These neutral solvents might be expected to give truly physical dispersions, but this does not seem to be the case. Beck (*22*) found that films prepared from a concentrated solution of calcium thiocyanate at 120° C. had less strength than the films prepared from viscose or cuprammonium solution from which he concludes that degradation had taken place. Sorption measurements by Sheppard and Newsome (*206*) and X-ray measurements by Katz and Derksen (*115*) on cellulose swollen in lithium thiocyanate solution indicate that the "hydrate" form of cellulose is obtained upon precipitation from salt solutions.

SPECIAL SOLVENTS

Lilienfeld (*134*) has taken out a patent for preparing solutions of cellulose in sodium hydroxide of 4- to 10-percent concentration at temperatures from +5° to −25° C. According to him, 8-percent sodium hydroxide scarcely dissolves mercerized cellulose at 0°, incompletely at −5°, and completely at −8°. According to the author's experience, however, native cellulose cannot be appreciably dissolved by this process and hydrated and partially degraded cellulose can be dissolved to form only relatively dilute solutions.

Sheppard (*203*) describes a process for mechanically dispersing cellulose by grinding it in organic liquids. Only a small part of the material becomes colloidally dispersed. The bulk of the material becomes similar to "hydrocellulose" obtained by the action of dilute acids.

Liquid ammonia solutions of a number of inorganic salts, such as iodides and thiocyanates, also act as dispersion media for both regenerated and native cellulose (*195*, *248*).

Fox (*67*) gives an interesting review of the dispersion of cellulose. He also considers viscose and the derivatives of cellulose which are not covered in this publication.

DEGREE OF DISPERSION

The classical methods for determining molecular weights, unfortunately, have been of little value in studying cellulose dispersions. As was shown under the discussion of X-ray crystal structure, the micellar structural building units are of large colloidal dimensions. These, it is true, may disintegrate upon being dispersed, but all physical evidence indicates that the dispersed cellulose retains colloidal dimensions.

Conflicting opinions exist as to whether these large dispersion units can be considered molecules in the chemical sense or whether they should be considered molecular only in the physical sense. It is thus preferable to think of the molecular weights considered here as particle weights, although evidence is accumulating to the effect that these materials exist as macromolecules in a chemical as well as the physical sense.

Osmotic pressure measurements have been recently applied in the study of the molecular weight of cellulose derivatives in organic solvents by Duclaux and Nodzu (*53*) and by Büchner and Samwel (*33*) but no classical method has thus far been successfully used in the study of cellulose itself. Molecular weight values ranging from 18,000 to 60,000 were obtained by these investigators. Haworth and Hirst (*83*) by analytical means determined the amount of tetramethyl glucose in hydrolyzed completely methylated cellulose from which they conclude that the cellulose molecule is made up of chains of 100 to 200 glucose units which correspond to a minimum molecular weight of 20,000 to 40,000.

DIFFUSION MEASUREMENTS

Herzog and Krüger (*90*) made diffusion measurements on cuprammonium solutions of cellulose from which a molecular weight of 500,000 was calculated, using Einstein's diffusion law:

$$D=\frac{RT}{N}\times\frac{1}{6\eta\pi r_p} \tag{12}$$

in which D is the diffusion constant, R the gas constant, T the absolute temperature, η the viscosity of the solvent, and r_p the radius of the diffusing particle. Einstein's equation was derived for the simple case of spherical particles in dilute solution in which the diffusion of a particle is unhindered by the presence of other particles. X-ray evidence has shown that the cellulose micelles are highly elongated. Other physical measurements, such as viscosity, further show that this rod shape is retained when cellulose is dispersed. These diffusion measurements were made at cellulose concentrations of about 1 percent. Such concentrations are undoubtedly too high for free diffusion to take place. Because of these limitations it is questionable if the measurements give more than the rough order of magnitude of the molecular weight. The result is perhaps sufficiently accurate, however, to disprove the false conception given by early X-ray evidence that the unit cell of four glucose units corresponds to the molecular weight.

ULTRACENTRIFUGE MEASUREMENTS

The author obtained more direct evidence of the high molecular weight of cellulose dispersed in cuprammonium solvent by means of the Svedberg ultracentrifuge (*223*). Measurements of the molecular weight were made by the sedimentation velocity method in a high centrifugal field in which the force of gravity was increased over one-hundred-thousandfold. By photographically following the changes of the index of refraction of the sedimenting system at different distances from the center of rotation with time, the rate of motion of the sedimenting boundary and the extent of diffusion across that boundary were determined. From these sedimentation velocity and diffusion measurements the molecular weight can be calculated independent of the use of Stokes law of settling, which applies only for spherical particles, using the following relationship:

$$M=\frac{RTs}{D(1-v\rho)} \qquad (13)$$

in which M is the molecular weight, R the gas constant, T the absolute temperature, s the sedimentation velocity per unit of centrifugal force, D the diffusion constant, v the partial specific volume of sedimenting material, and ρ the density of the solvent. These measurements also indicate whether the material is mono- or poly-disperse from the symmetry of the refractive index-height curves. Centrifugal measurements made with different concentrations of cellulose ranging from 0.02 to 0.5 percent showed a slight increase in the sedimentation velocity and a very decided increase in the diffusion constant with a decrease in concentration, thus showing the low concentrations necessary for free diffusion. Molecular weights were hence calculated from values of S and D extrapolated to zero concentration. Cotton linters alpha cellulose was found to be monodisperse and to have a molecular weight of 40,000 ± 5,000.

These measurements do not give any direct evidence of the shape of the dispersed particles. From the low concentrations necessary to obtain free diffusion it is obvious, however, that the particles must be quite unsymmetrical. If the dispersed particles were spherical, the average distance between particles in the 0.5-percent solution would be 4.5 times their diameter. If the length of the dispersed particles is 500A, the length found from the X-ray crystal lattice by the spreading of the diffraction rings, and the sphere of influence has a diameter equal to this particle length, the spheres of influence will overlap considerably in a 0.5-percent solution. In a 0.05-percent solution the spheres of influence will be tightly packed and in a 0.01-percent solution the distance between the spheres of influence will be just 0.75 times their diameter. This is in harmony with the experimental diffusion concentration curves which indicate that free diffusion does not take place above a concentration of 0.01 to 0.02 percent.

Measurements of the molecular weight were also made by the sedimentation-equilibrium method. In this case only a sufficient centrifugal force is required to give a measurable concentration change with height in the cell resulting from an equilibrium between the rate of settling of the dispersed particles and their diffusion in the opposite direction. The molecular weight is dependent merely on the concentration-height relationship

$$M=\frac{2RTln(c_2/c_1)}{(1-v\rho)\omega^2(x_2^2-x_1^2)} \tag{14}$$

in which c_2 and c_1 are the concentrations at distances from the center of rotation of x_2 and x_1, respectively, ω is the angular velocity of the centrifuge and the other symbols have the same meaning as heretofore. Two determinations made by this method on the cotton linters alpha cellulose gave practically the same molecular weight as was obtained by the sedimentation-velocity method. Recent measurements by Kraemer and Lansing (*124*) give higher molceular weight values (p. 86). The reason for this difference has not yet been determined.

The molecular weights of several wood celluloses were determined by the sedimentation-velocity method (*224*). In all cases the cellulose was polydisperse. A molecular weight constituent the same as that of cotton linters alpha cellulose was present, together with varying proportions of lower molecular weight constituents. This is in harmony with chemical and viscosity evidence. Purified wood cellulose is chemically identical with cotton cellulose but its reactivity is greater and its viscosity lower.

VISCOSITY MEASUREMENTS

Considerable effort has been made to characterize cellulose by means of the simple viscosity measurements. Unfortunately, the viscosity is dependent upon a number of factors, such as the state of aggregation of the dispersed particles, their shape, solvation, and electroviscous effect in electrically conducting media. In spite of these complications viscosity measurements in cuprammonium solution have been satisfactorily used as an empirical means of determining the condition of cellulose. Native cotton cellulose gives higher viscosity values than isolated wood celluloses and higher values than various degraded celluloses. The viscosity of a cellulose in cuprammonium solution is further an index of the fiber strength (*42, 188*) and also of the viscosity of nitrocellulose or cellulose acetate solutions that can be made therefrom (*103, 104*). Because of this, viscosity measurements have found an important place in industry as a means of controlling cellulose products.

Einstein (*56, 57*) has derived an equation for the viscosity of a dilute solution of spherical particles, η_c, in terms of the concentration expressed as the partial specific volume, ϕ.

$$\eta_c=\eta(1+2.5\phi) \tag{15}$$

in which η is the viscosity of the solvent, or

$$\eta_{sp}=2.5\phi \tag{16}$$

in which η_{sp} is the increase in relative viscosity caused by the solute. According to these equations the viscosity is independent of the nature and state of dispersion of the solute. The relationship holds for glucose and sucrose solutions up to a concentration of about 10 percent and for gamboge suspensions up to 2 percent (*236*). For considerably elongated molecules, such as cellulose and its derivatives, the deviation from this relationship is large, even in fairly dilute solutions. This deviation is presumably due to the fact that the sphere of influence of a freely moving elongated particle is many times the particle volume, whereas it is equal to the particle volume for spherical particles. Onsager (*170*) has worked out the case of rotation ellipsoids and has found that the factor 2.5 in Einstein's equation increases with the square of the ratio of major to minor axis. This is nearly equivalent (differing by the constant factor 0.33 for cylindrical rods) to considering the effective particle volume equal to the sphere of influence with the particle length as the effective diameter.

Staudinger (*236*, *238*) has shown that the empirical relationship

$$\eta_{sp}=k_m cM \text{ or, } \eta_{sp}=k_l cL \tag{17}$$

where c represents the concentration, M the molecular weight, L the particle length, and k_m and k_l are constants characteristic for each homologous series and solvent, holds very well for long-chain polymers up to a molecular weight of 10,000. The molecular weights in these cases can be checked by the classical methods. Staudinger has also attempted to extend the relationship to the measurement of the molecular weight of cellulose and rubber (*235*, *236*, *237*, *239*, *240*). This procedure has been questioned by Mark (*144*) and by Kraemer and Van Natta (*125*). Not only are the actual viscosity measurements questionable because of the deviations from the Hagen-Poiseuille flow law with these exceedingly long-chain molecules (*187*), but further there is a considerable deviation from the linear viscosity-concentration relationship at even relatively low concentrations, the viscosity increasing more rapidly than the relationship predicts. In his earlier estimations of the molecular weight, Staudinger determined the constant k_m for cellulose from the viscosity and classical molecular weight measurements on degradation products of cellulose which he had to assume were still homologues of the original cellulose (*236*). More recently he has used values of k_m obtained by making a correction for the amylene oxide ring structure (*237*) on the basis of the general finding that—

> when normal with respect to the chain equivalent weight, solutions of polymeric hydrocarbons having the same molecular weight have the same specific viscosity, independent of the structure of the molecules.

From these deductions Staudinger gives a molecular weight value for cellulose of 120,000 and a chain length of 3,900A, considering the chains as single macromolecules. These measurements are still rather speculative, but they do indicate that there must be a relationship between viscosity and the length of the molecular chains.

Ekenstam (*58*) has determined the viscosity of cellulose in concentrated acid solutions. In all cases the viscosity decreased with time as would be expected due to the degradation of the cellulose. Viscosity measurements of cotton dissolved in phosphoric acid when extrapolated to zero time and zero concentration gave a molecular weight of 340,000 using the above relationships of Staudinger.

X-RAY MEASUREMENTS

Mark (*144*) believes that the dispersion units of cellulose are of the same magnitude as the micellar units found in the solid crystal lattice, namely, 500A by 50A, which corresponds to a molecular weight of about 1,000,000. He showed that the spreading of the X-ray diffraction rings of regenerated cellulose does not depend on the rate at which the cellulose is regenerated from solution. If the solid crystal lattice micellar units were further disintegrated on solution, the rate of regeneration should affect the extent to which they can reaggregate and hence their size.

SPREADING MEASUREMENTS

A number of measurements have been made on the spreading of cellulose derivatives on mercury by Sheppard and Keenan (*205*) and on water by Katz and Samwel (*117*) and by Adam (*1*). All these measurements give a film thickness practically the same as the thickness of a single glucose chain obtained by X-ray measurements. Adam attempted to make the measurements with a cuprammonium solution of cellulose, but precipitation rather than spreading occurred on the water. It is quite probable, however, that the results would not differ appreciably from those obtained with cellulose derivatives. The cellulose molecules presumably lie flat on the surface due to the multipolar structure rather than exhibiting the end-on orientation shown by such bipolar molecules as fatty acids. The results also show that cellulose and its derivatives must either be dissolved as single molecular chains according to Staudinger, or the bundles of chains must be internally sufficiently mobile to open up on the liquid surface.

These various values for the size of the dispersion units of cellulose do not agree so well as might be desired, but it should be noted that they do not all measure the same thing (p. 86). The osmotic pressure and ultracentrifuge methods give molecular weights of the dispersed cellulose directly, the analytical and the viscosity measurements give primary chain lengths, the diffusion measurements give average effective dimensions, the spreading measurements give cross-sectional thickness, and the X-ray measurements give both length and cross-sectional thickness for the cellulose units in the solid lattice. Kraemer and Lansing (*124*) have pointed out that the ultracentrifuge, diffusion, and viscosity methods give "weight average molecular weights" whereas the osmotic pressure gives a "number average molecular weight." In the case of polydisperse systems the latter method should give lower molecular weight values than the others. None of the methods gives positive evidence of the dispersion as bundles of chains but the spreading measurements give positive evidence and the viscosity measurements partial evidence that the chains are each individually dispersed. All the measurements with the exception of the uncertain diffusion measurements give chain lengths ranging from 100 to 800 glucose units on the basis of dispersion as single chains. On the basis of dispersion in bundles the osmotic pressure and ultracentrifuge methods would give still shorter chain lengths, thus increasing the divergence between the values obtained by the different methods. The evidence thus predominantly indicates that the dispersion units consist of single primary valence chains that can be considered as macromolecules.

ELECTRICAL CONDUCTIVITY

Fibrous materials themselves are good electrical insulators, their conductivity depending almost entirely upon adsorbed films of moisture. Clark and Williams (*41*) obtained specific conductivities for several species of dry wood of the order of 10^{-18} mho. This value compares favorably with the value for the best insulators. Curtis (*46*) and Kujirai and Akahira (*127*) have determined the effect of the moisture content on the electrical conductivity of various fibrous materials. Hiruma (*98*), Hasselblatt (*80*), and the author (*217*, *219*, *222*) have made similar measurements on wood, and Walker (*159*, *270*, *271*) and his associates have made extensive measurements on cotton. In all cases the conductivity increases very rapidly with an increase in moisture content up to the fiber-saturation point (p. 86). The author found an approximately linear relationship to hold between the moisture content and the logarithm of the electrical conductivity of wood from 7-percent moisture content to the fiber-saturation point, which, in general, is 30-percent moisture content. The conductivity change over this range is over a hundred thousandfold. From the fiber-saturation point to the completely water-filled condition, which varies from a moisture content of approximately 150 to 300 percent, depending on the density of the wood, the conductivity change is only about twentyfold. The author has used this sharp break in the conductivity-moisture content relationship as a means of determining the fiber-saturation point (*219*). The great change in electrical conductivity with changes in moisture content below the fiber-saturation point has also been used by the author (*217*, *222*) as a means of determining the moisture content of wood. Such variables as species, density of the wood, and variations in ash content all have an inappreciable effect on the conductivity when compared with the effect of the moisture content. A practical instrument for measuring the moisture content of wood based on these findings has been developed by Suits and Dunlap (*246*). Walker found that the electrical conductivity of cellulose fibers can best be expressed with three different functions. Below 3-percent moisture content the logarithm of the conductivity varies linearly with the moisture content, between 3- and 10-percent moisture content the logarithm of the conductivity varies linearly with the logarithm of the moisture content, and from a moisture content of 10 to 23 percent the logarithm of the conductivity varies linearly with the relative humidity.

All of these fibrous materials give a hysteresis loop when a function of the electrical conductivity is plotted against the relative humidity. On desorption the conductivity is greater than on adsorption. Practically no hysteresis exists in the conductivity-moisture content relationship, however. The hysteresis effect will be considered more at length under the heading of Sorption of Water Vapor and Sorption Hysteresis (p. 40).

SURFACE CONDUCTIVITY

Briggs (*28*) has quantitatively studied the surface conduction of cellulose. He obtained a surface conductivity using distilled water that was on the average about 10 times that of the bulk conductivity. Very dilute salt solutions showed an increase in the surface conductivity with an increase in bulk conductivity. The ratio of the surface conductivity to the bulk conductivity decreases in more concentrated solutions and becomes negligible in approximately 0.1 normal salt solutions. A lyotropic effect was obtained with a series of chloride salts, the NH_4+ ion giving a greater surface conductivity than the $Li+$ ion. No relationship between the ζ potential and the surface conductivity was obtained. Briggs believes that the generally accepted explanation that surface conduction is due to conduction along the Helmholtz double layer is invalid. He offers as an alternate explanation the possibility of a displacement of the polyhydrol water equilibrium toward the monohydrol form by adsorption on the cellulose surface and a greater conductivity of the monohydrol than of the normal water.

Kanamaru (*105*) determined the surface conductivity of pulp beaten to different degrees. The unbeaten pulps showed surface conductivities using distilled water that ranged from 10 to 20 times the bulk conductivity. Beating the pulp increased the surface conductivity in the order of 50 percent.

The specific conductivity of wood at the fiber-saturation point, according to the author's data (*219*, *220*) is, in general, 10 times the conductivity of the same amount of water in bulk. This difference may, in part, be due to soluble electrolytes that cannot be readily washed out from the wood structure but it is highly probable that a large part of this difference in conductivity is due to surface conduction.

ELECTROKINETIC PHENOMENON

ζ POTENTIALS

Any solid in contact with a liquid assumes an electrical charge with respect to the liquid as a result of selective adsorption of ions. The oppositely charged ions become immobilized in the bulk solution in close proximity to the adsorbed ions in order to maintain electrical neutrality. The electrokinetic potential set up between the adsorbed ions and the bulk of the solution is known as the ζ potential. Cellulose, as well as other fibrous materials, has a negative ζ potential with respect to water. Harrison (*76*, *78*) made the first quantitative measurements on cellulose by the streaming-potential method. He appreciated the effect of surface conduction and hence determined the conductivity of his water and solutions in the cellulose membranes. Using the equation of Helmholtz,

$$\zeta=(300)^2\frac{4\pi\eta\kappa E}{PK}=(300)^2\frac{4\pi\eta V}{EKq} \qquad (18)$$

in which η is the viscosity of the liquid, κ the specific electrical conductivity of the liquid in the capillary structure, E the difference in electromotive force between the ends of the tube or across the section, P the applied hydrostatic pressure, K the dielectric constant of the liquid, V the velocity of electro-osmose, and q the effective capillary cross section, he obtained a value of 0.0157 volts for the ζ potential of his cellulose against distilled water. Briggs (*29*) in his extensive streaming-potential measurements on cellulose obtained ζ potential values of 0.0214, 0.0161, and 0.0083 volts for two different kinds of filter paper, and a sulphite pulp against water. Kanamaru (*105*) studied the effect of beating a standard cotton cellulose and a sulphite pulp upon the ζ potential obtained by streaming-potential measurements. The ζ potential of the standard cotton increased from 0.029 to 0.045 volts on beating for 216 hours, whereas the sulphite pulp gave an increase in ζ potential from 0.012 to 0.018 volts. The author (*215, 218, 220*), using the method of electro-osmose, obtained ζ potential values for different woods against water averaging 0.014 volts (p. 86).

EFFECT OF ELECTROLYTES

Small concentrations of electrolytes have been shown by Briggs (*30*) in his streaming-potential measurements on cotton cellulose, by the author (*216*) in electro-osmotic measurements on wood sections, and by Lottermoser (*135*) in electrophoratic measurements on suspended wood flour, to affect the ζ potential in a similar manner to the effect of electrolytes upon the ζ potential of other colloidal materials that are negatively charged with respect to water. Briggs found that monovalent cations with the exception of hydrogen increase the negative ζ potential up to concentrations of 0.1 milliequivalent. Above this concentration the ζ potential decreases. The effectiveness of the cation chlorides in increasing the ζ potential is in the lyotropic series order: $Cs < K < Na < Li$. Hydrogen ions, on the other hand, caused a decrease of the ζ potential over the whole range of concentrations. The increase in the ζ potential at low concentrations was found to be greater for the chloride ion than for the acetate ion. Briggs explains the change in the effect of monovalent cation chlorides with concentration as due to a combination of two different concentration-free energy effects.

> The one more pronounced at lower concentrations is due to the preferential adsorption of chloride ions, this being overshadowed at higher concentrations by that due to the cation part of the molecule.

Briggs' data do not show the original increase in ζ potential at low concentrations for bivalent cations but they do show the decrease at lower concentrations than that at which a decrease is obtained with monovalent ions. The trivalent cation, aluminum, showed a more marked decrease in ζ potential with an increase in concentration than was shown by the bivalent ions. The ζ potential became zero at relatively high concentrations. Thorium, a tetravalent cation, gave a zero ζ potential at about 0.3 milliequivalents and then a large increase in positive ζ potential with further increase in concentration. Briggs also showed that beyond the optimum points the ζ potential shows a linear relationship with the logarithm of the concentration.

Lottermoser (*135*) and the author (*216*), in general, obtained similar results with wood except that the increase in ζ potential with monovalent ions continued to higher concentrations. The bivalent cations further gave an initial increase in negative ζ potential up to concentrations of 0.5 to 1 milliequivalents before giving a decrease. Aluminum ions also caused a zero ζ potential at lower concentrations (0.2 to 0.3 milliequivalents) followed by an increase in positive potential. Thorium ions gave a zero ζ potential at 0.1 to 0.3 milliequivalents followed by a considerable increase in positive ζ potential.

The author (*216*) found the negative ζ potential in the case of wood to increase with an increase in the pH. In alkaline solutions the effect was reversible. When the alkali was washed out the original negative ζ potential was obtained, but when the solution was made acid a permanent decrease in the negative ζ potential resulted which is very likely caused by surface hydrolysis. The acid-alkali isoelectric point is thus meaningless for cellulosic materials as it would be in solutions so acid that normal cellulose could not exist.

Bull and Gortner (*34*, *35*) found that the ζ potential of cellulose against water has practically a negligible temperature coefficient and that mixtures of dilute salt solutions give average effects and show no ion antagonism.

NONAQUEOUS SYSTEMS

Strickler and Mathews (*245*) made electro-osmose measurements in nonaqueous media, using filter-paper membranes. Their data are, however, unsuitable for calculating ζ potentials. Martin and Gortner (*148*) determined the ζ potential of cellulose in nonaqueous media by streaming-potential measurements. They found that the ratio of the electromotive force to the pressure applied increased with increasing pressure up to a final constant value. Pressures sufficient to give this constant ratio were used in determining the ζ potentials. The ζ potential was found to be a function of the molecular structure and polarity of the liquid. Symmetrical benzene gave no ζ potential and toluene the small value of -0.2 millivolts. When other groups were substituted for hydrogen in the benzene ring the following order of increasing negative ζ potential values was obtained:

$$H < CH_3 < Cl < Br < NH_2 < NO_2$$

Nitrobenzene gave the largest ζ potential obtained, namely, -142 millivolts (p. 89). Methanol gave a negative potential of 55.3 millivolts. The addition of CH_2 groups up to and including n-butanol decreased the negative potential by 36 millivolts, whereas the substitution of a methyl group for a hydrogen atom to form a branched chain altered the ζ potential by only ± 4 millivolts.

ADSORPTION OF SOLUTES

ADSORPTION OF ALKALIES

Evidence on the adsorption of solutes from solution by cellulose is very conflicting. Mercer, as early as 1844, believed that alkalies form chemical compounds with cellulose. He has been supported in this view down to the present time by Gladstone (*72*), Thiele (*249*), Viewig (*267*), Kolthoff (*122*, *123*), Hess (*92*, *94*, *95*), and others. Miller (*153*), Leighton (*132*), Joyner (*104*), and Bancroft and Calkin (*10*), on the other hand, view the process from a colloid chemical standpoint as an adsorption phenomenon.

There is not only a difference among investigators in the interpretation of data, but also a difference in the data obtained from similar measurements. Gladstone treated cotton with strong sodium hydroxide and washed it with cold absolute alcohol or hot alcohol of 0.825 specific gravity. The alkali remaining in the fiber agreed with the formula $(C_6H_{10}0_5)_2$ NaOH; hence he considered it combined. Hübner and Teltscher (*100*) were, however, able to wash all of the sodium hydroxide from cotton with hot absolute alcohol. Viewig (*267*) treated cotton with solutions of sodium hydroxide of various concentrations and determined the amount of alkali absorbed by titrating a portion of the liquid. On plotting the amount of sodium hydroxide absorbed against the concentration of the original solution two definite breaks occurred in the curve at 16- and at 35-percent concentration, corresponding to 13- and 24-percent absorption and ratios of $(C_6H_{10}O_5)_2$:NaOH and $(C_6H_{10}O_5)_2$:2NaOH, respectively. Miller (*153*) followed practically the same procedure as Viewig but obtained no breaks in the curve. Leighton (*132*) correctly pointed out the fact that Viewig was measuring absorption and not adsorption because of the liquid taken up by the capillaries. He centrifuged his cotton after treating with alkali to remove the free liquid before analysis. Below a concentration of 9 percent he obtained no adsorption, and at higher concentrations no sign of chemical reaction. According to Kolthoff, cellulose takes up sodium hydroxide in accordance with the partition law from solutions up to 8-percent concentration. Between 8 and 24 percent, the amount taken up increases greatly but is independent of the concentration, while at 32 percent there is another decided increase in the amount taken up which is also independent of the concentration.

Neale (*163*) has critically studied the action of sodium hydroxide on cellulose by determining the distribution of sodium hydroxide between cellulose and water, the subsequent swelling, and the heat of reaction. He concludes that cellulose may be considered as a weak monobasic acid and calculates its ionization constant to be approximately 2.0×10^{-14} at 25° C. He further concludes that the alkali is taken up to form a salt according to the law of mass action and without chemical reaction in amount required to satisfy the Donnan equilibrium.

Bancroft and Calkin (*10*) in their recent study of cellulose-alkali solution systems have shown that when the amount of water taken up with the alkali is properly accounted for there is no indication of compound formation. They find that the results can be entirely explained on the basis of adsorption.

The concentrations necessary for maximum swelling of cellulose in the different alkalies are, according to Heuser and Bartunek (*96*), LiOH 9.5 percent, NaOH 18, KOH 35, RbOH 38, and CsOH 40 percent. The stoichiometric proportions in which the alkalies are taken up are 1 mole of alkali to 2 of glucose for the first three alkalies and 1 mole of alkali to 3 of glucose for the two latter alkalies.

This conflicting evidence on the action of alkalies on cellulose can, in part, be explained by the recent X-ray evidence which shows no change in the X-ray lattice below a minimum alkali concentration of about 10 percent. Taking up of alkali by cellulose below this concentration would, consequently, be due to a surface adsorption or reaction rather than stoichiometric combination as the interior of the micelles is not available for the solute. As the concentration of the alkali is increased, the lattice changes indicate an intramicellar change. The interior surface of the micelles supposedly becomes more and more available and consequently adsorption or surface reaction increases. When all the internal surface becomes available, then and only then can the addition of alkali be considered as a true stoichiometric chemical reaction. This may be the case only under conditions of optimum swelling.

Harrison (*77*) attributes failure to follow the ordinary adsorption equation to the change in physical state of the fiber. With regenerated cellulose, maximum absorption of water and sodium hydroxide take place in a 9-percent alkali concentration while with cotton a 17.5-

percent solution of sodium hydroxide is required for maximum absorption. This difference, he believes to be due to the resistance to swelling of the cotton cuticle.

ADSORPTION OF ACIDS

Acids are only slightly adsorbed by cellulose from dilute solutions. Kolthoff (*122, 123*) found that the adsorption of hydrochloric, sulphuric, acetic, and oxalic acids from 0.1N solutions was very small and practically equivalent to the alkalinity of the cellulose ash. Mokruschin and Kryloff (*156*) also found the adsorption of acids to be very small and the maximum adsorption to be attained in low concentrations. They explain this on the basis of the electrical theory of adsorption. At moderate concentrations there is no evidence of compound formation.

Kanamaru (*106*) determined the adsorption by cellophane of hydrogen and hydroxyl ions from dilute acid and alkali solutions of different pH value from the difference between the initial and the equilibrium hydrogen-ion concentrations. Hydrogen ions were adsorbed in excess of the water at pH values below 7.4 and hydroxyl ions were adsorbed in excess at pH values above 7.4. Appreciable ion adsorption occurred only above a pH of 11. The pH at which ions and solvent are adsorbed in the same proportions in which they exist in solution Kanamaru calls the "apparent isoelectric point" or "hylotropic adsorption point." This point is shown to vary with the previous treatment of the cellophane.

ADSORPTION OF SALTS

Adsorption of salts from dilute solution by wood was found by the author (*221*) to be very small and of a selective nature. A slight positive adsorption of cations was obtained from $BaCl_2$ and $AlCl_3$ and a negative adsorption of chloride ions from NaCl, $BaCl_2$, and $AlCl_3$. According to Percival, Cuthbertson, and Hibbert (*178*), $Al(OH)_3$ is positively adsorbed by ash-free cellulose in small but definite amounts from the chloride, sulphate, and acetate salts. It is greatest from the latter because of the increased tendency for hydrolysis. Lottermoser and Hönsch (*136*) studied the adsorption of salts from concentrated solution on cellulose. From the concentration change of the anion they found positive adsorption of NaCl, KCl, $CaCl_2$, and KCNS and a negative adsorption of LiCl. Optimum adsorption required about 30 hours. The final equilibrium adsorptions were, in general, somewhat less.

SORPTION OF ORGANIC SOLUTES

Practically all sorption measurements of organic solutes on cellulosic materials have been made with dye solutions from a practical dyeing standpoint. Most of the investigations are outside of the realm of this publication. The data are in general difficult to interpret. Solute and solvent are in most cases simultaneously absorbed. The dyes themselves are largely collodial in nature and whether they are accessible to all the structure to which water is accessible is questionable. Then, too, in dyeing processes salts are added. Some investigators such as Morton (*157*) believe that the salt increases the degree of dispersion of the dyes. Robinson (*157, p. 277*) in the discussion of Morton's paper (*157*) suggests that the effect of salts may be entirely electrokinetic in nature and serve merely in aiding transport of the dye. In general, basic dyes are taken up better by cellulose than are acid dyes. Ando (*5*) has shown that the adsorption of methylene blue by cellophane increases with an increase in concentration according to Freundlich's adsorption equation. The adsorption decreases linearly with a decrease in pH of the methylene blue solution. The adsorption is affected by the presence of salts. Neale and Stringfellow (*165*) studied the absorption of sky-blue FF by cellophane and showed that the taking up of the dye is a diffusion process. Absorption of the dyestuff from pure aqueous solution was negligible but it increased rapidly upon the addition of salt.

Measurements of Barkas (*11*) show that sugar is negatively adsorbed from aqueous solution. Glucose [8] has also been shown to be negatively adsorbed from solution by wood.

Sorption from nonpolar solvents, although, in general, quite small because of the reduced surface, seems to be quite specific. Preliminary measurements of the adsorption of stearic acid by wood from a benzene solution made by the author indicate that the adsorption increases with concentration up to a saturation value. Calculation of the extent of the adsorbing surface assuming that the adsorption is monomolecular gives a value about four times that of the calculated surface of the fiber cavities. This value is, of course, small in comparison with the internal surface of the swollen material.

SORPTION OF GASES AND VAPORS

SORPTION OF GASES

Davidson (*47*) showed, as a result of his measurements of the specific volume of cotton cellulose in helium gas, that helium was negligibly adsorbed because it gave the same specific-volume values at different applied pressures. With this as a basis he found air to be adsorbed to the extent of 0.023 cc per gram of dry cellulose under standard conditions. The author (*221*) in making similar measurements on wood found that hydrogen was adsorbed to the extent of 0.013 cc, nitrogen 0.020 cc, and oxygen 0.042 cc per gram of dry wood under standard conditions. The sorption of nonpolar gases by cellulosic materials is thus very small (p. 87).

Larger values have been obtained for the sorption of polar gases (p. 87). Grace and Maass (*73*) have determined the sorption of dry hydrochloric acid, sulphur dioxide, and ammonia gases on dry cotton and dry white spruce wood. Cotton sorbed 0.8 percent of hydrochloric acid gas at 5.4 cm of mercury pressure and 2.0 percent at 70.2 cm of mercury. The wood sorbed 3.2 percent at 5 cm of mercury pressure and 10.5 percent at 75 cm of mercury. There seemed to be no sorption hysteresis as in the case of the sorption of water vapor. In the presence of water the sorption of hydrochloric acid gas, corrected for that held by the water, decreased slightly with an increase in moisture content up to about 3 percent and then increased. Sulphur dioxide was sorbed by cotton to the extent of 5 percent at 76 cm of mercury. This was reduced only to 0.8 percent by evacuating for 3 days at room temperature. At 85° C. it was readily removed, however. The sorption on the wood was still greater, 13.6 percent being sorbed at 76 cm of mercury pressure. Evacuation for 1 day at room temperature reduced this to 4 percent. At 85° it was also readily removed. Ammonia was sorbed to the extent of 4 percent by cotton and 7.4 percent by the wood at 76 cm of mercury pressure. All three of these gases reached sorption equilibrium with wood in 10 to 12 hours, whereas 50 to 100 hours were required for cotton. Carbon dioxide was sorbed only to the extent of 1 percent by the wood at 42 cm of mercury pressure. No increase in sorption occurred on increasing the pressure to 76 cm of mercury.

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[8] SALZBERG, H. K. EFFECT OF PINE SAWDUST ON SOLUTIONS OF MERCURIC CHLORIDE, AMMONIACAL COPPER SULPHATE, AND GLUCOSE. U. S. Dept. Agr. Forest Prod. Lab. Project 269, 6 pp. 1927. (Typewritten report.)

SORPTION OF WATER VAPOR AND SORPTION HYSTERESIS

The relationship between the moisture content of textiles and the amount of moisture in the atmosphere was perhaps first fully appreciated by Mueller (*158*) who in 1882 worked out an equation containing two constants to express the relationship. Schlœsing (*196*) determined the moisture regain-relative humidity relationship of cotton from different sources by passing humidified air through the material until equilibrium had been attained and then determined the humidity of the air by absorption in sulphuric acid. He also used the sulphuric acid desiccator method.

Masson and Richards (*149*) by means of the sulphuric acid desiccator method obtained the characteristic sigmoid moisture content-relative vapor-pressure curves for cotton in which the rate of increase in moisture content with increasing relative vapor pressure decreases to a minimum and then increases to a maximum at the fiber-saturation point, the moisture content below which the activity of the water is less than unity. They observed that a different moisture equilibrium is obtained if equilibrium is approached from a higher relative vapor pressure than when approached from a lower relative vapor pressure. These differences were at the time attributed to the incomplete attainment of equilibrium rather than to true hysteresis.

Kujirai, Kobayashi, and Toriyama (*128*), working with a number of different fibrous materials, obtained typical sorption curves with a definite hysteresis effect in each. The points obtained by desorption gave larger equilibrium moisture-content values than those obtained by adsorption at the same relative vapor pressure.

Urquhart and Williams (*257*, *262*, *263*, *264*, *265*) have carried out extensive sorption measurements on cotton. They used a modification of the vacuum method of Trouton (*256*). Vapor pressures were read on a manometer connected directly to the sample tube. Water vapor was admitted from a small calibrated pipette for adsorption measurements and removed by a P_2O_5 tube, which could be disconnected for weighing, in desorption measurements. With this appratus in which the air pressure was reduced to as low as 0.001 mm of mercury, the same sorption hysteresis loop extending from very low relative vapor pressures to saturation was obtained as that found by making the measurements in air.

Measurements of the moisture content-relative vapor-pressure relationship of cotton and wood were made by Pidgeon and Maass (*180*), and of wood pulps by Campbell and Pidgeon (*38*), using an evacuated system in which the sorption was determined by following the changes in weight of the material suspended from a quartz helix balance, the extension of which was measured with a cathetometer. These investigators also obtained the normal sorption curves and hysteresis effect.

Seborg and the author determined the moisture sorption by wood and wood pulps under atmospheric conditions by circulating air humidified in saturated salt solutions over specimens suspended from quartz helix balances. Similar sorption curves to those obtained by other investigators were obtained. A hysteresis sorption loop was obtained for wood within which all available controlled drying data on larger specimens fell (*233*). The drying under industrial controlled conditions of larger wood specimens in which considerable moisture gradients are set up is quite similar to drying under oscillating humidity conditions. Such conditions would be expected to give intermediate values.

Mörath (*155*) reports measurements on several different species of wood made by passing air over wood sawdust after it was humidified by bubbling through sulphuric acid of different concentrations. Similar curves to those previously described were obtained. The hysteresis effect was, however, less marked, undoubtedly due to imperfect temperature control (to 1° C.).

Knight and Pratt (*119*) have further studied the sorption hysteresis for moderately sized wood specimens conditioned in humidity chambers. Readsorption measurements after drying the specimens over phosphorous pentoxide at 50° C. and oven drying at 100° showed that higher equilibrium moisture-content values were obtained in the first than in the last case, even though the moisture content of each was calculated on the basis of the final oven-dry weight. When the desorption measurements were carried to 60-percent relative vapor pressure and the cycle from there on to 90-percent relative vapor pressure was repeated several times, a closed hysteresis loop with the desorption part practically coinciding with the original desorption curve and the adsorption part intermediate between the lines representing the complete hysteresis loop was obtained. In a similar way hysteresis loops between 50- and 80-percent relative vapor pressure, 40- and 70-percent, and 30- and 60-percent were determined. The hysteresis loops for descending relative vapor-pressure cycles gave values for the desorption part of the curve deviating more and more from the complete desorption curve.

Urquhart and Eckersall (*260*) have critically studied the hysteresis loop. They found that the complete cycle hysteresis loop represents the boundaries of an equilibrium area, any point on which may represent the moisture sorption of the cellulosic material under suitable relative vapor pressure and preliminary treating conditions. Adsorption, after a partial desorption, gave curves crossing from the complete-cycle desorption to the complete-cycle adsorption curve of the hysteresis loop. Above 80-percent relative vapor pressure they found the desorption curve to depend upon the initial moisture content. A desorption started from the saturation point fell below one started from a considerably higher moisture content until 80-percent relative vapor pressure was reached. Below this point the two curves coincided.

Urquhart and Williams (*257*, *262*, *263*, *264*, *265*) also determined the effect of temperature on the adsorption of water vapor. For relative vapor pressures of less than 80 percent an increase in temperature from 10° to 110° C. decreases the moisture content of cotton at constant relative vapor pressure. For values of the relative vapor pressure greater than 80 percent an increase of temperature from 10°

to 50° decreases the moisture content also, but from 60° to 110° it increases the moisture content at constant relative vapor pressure. It is suggested that this increase of moisture content at constant relative vapor pressure above 60° is due to making available fresh surface for water sorption.

Data by Loughborough (*81*, *233*) on the drying of wood at different temperatures and relative vapor pressures from 21° to 100° C. do not show the above change in sorptive power. The data show a decrease in sorption with an increase in temperature over the whole relative vapor pressure range, and a linear decrease in the fiber-saturation point of about 0.1 percent for each degree centigrade increase of temperature.

Russell and Campbell[9] found that a previous thermal treatment affected the sorption of water vapor by pulp. Sample no. 1 was heated in water vapor at 100° C., no. 2 was heated in dry air at 100°, and no. 3 was untreated. When the pulps were saturated with water and desorption measurements made, the decreasing order of moisture content in equilibrium with the same relative humidity was samples nos. 1, 3, and 2. When the pulps were dried over phosphorous pentoxide at room temperature after the heat treatment the subsequent adsorption values in the order of decreasing sorption were samples nos. 3, 1, and 2.

Hysteresis loops extending from saturation to practically zero relative vapor pressures have been invariably found by cellulose investigators who worked with small specimens under carefully controlled conditions. In all cases the desorption shows higher moisture-content values than adsorption for the same equilibrium relative vapor pressures. Patrick (*172*) has attributed the hysteresis in the case of silica gel to the presence of adsorbed air. Pidgeon (*179*) has recently shown that the absence of a hysteresis loop in Patrick's measurements of the sorption of water vapor by silica gel was not due to the complete removal of air as he supposed, but due to the changing vapor pressure during sorption. Urquhart and collaborators (*257*, *258*, *260*, *262*, *263*, *264*, *265*) and Campbell (*37*) were further unable to reduce the hysteresis effects for cellulosic materials working under reduced pressures of 0.001 mm of mercury. It thus appears that the phenomenon of hysteresis is a characteristic property of cellulosic material-water vapor systems and cannot be attributed to outside effects.

Zsigmondy's (*280*) explanation of the hysteresis loop on the basis of a difference under adsorption and desorption conditions in the curvatures of the menisci of the liquids filling the capillary spaces is also hardly applicable to elastic gels such as cellulose. Urquhart and Williams (*258*) explain the effect in a more plausible way for cellulose in which the swelling follows adsorption from the start. They attribute the effect to the condition of the secondary valence bonds of the hydroxyl groups of the cellulose molecules. In the original water-soaked condition the free hydroxyl groups are practically all satisfied by water. When the cellulose is dried these hydroxyl groups are freed and, as a result of the shrinking, pairs are drawn together so that the individual groups of adjacent cellulose molecules mutually satisfy each other. Upon adsorption part of the hydroxyl groups that have mutually satisfied each other are not freed for water adsorption, thus giving a decreased adsorption. This explanation of hysteresis is in harmony with a number of other observations of Urquhart and Williams, namely, that hysteresis decreases with an increase in temperature, that cotton taken directly from the plant gives a higher desorption curve than the same cotton after drying in an oven and resoaking (*260*), and that heating in water or steaming gives higher subsequent desorption curves than when the cotton is previously just brought to the fiber-saturation point. The apparent difference in the effect of temperature upon sorption obtained by Urquhart and Williams (*257*, *262*, *263*, *264*, *265*) and Loughborough (*81*, *233*) can also be explained on the basis of this theory. The increase in the hydroscopicity of cotton above 60° C. and 80-percent relative vapor pressure in adsorption measurements obtained by the former investigators would be due to part of the hydroxyl groups which mutually satisfied each other in the dry cellulose, being freed for water sorption above this temperature and relative vapor pressure. Loughborough's measurements, on the other hand, are desorption measurements on green wood in which the maximum number of hydroxyls are free for the binding of water. These could not be made to satisfy each other mutually until the wood was practically dry.

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[9] RUSSELL, J. K., and CAMPBELL, W. B. DEFINITION OF PULP QUALITY: HYGROSCOPIC QUALITIES OF PULP. Quart. Rev. Pulp and Paper Lab., Forest Prod. Lab. Canada No. 6 April–June 1931): 17–26. 1931. [Mimeographed.]

Another phenomenon perhaps related to the hysteresis is the Von Shroeder effect. Elastic gels, including cellulosic materials, show a greater sorption of water and consequent swelling when immersed in liquid water than when brought to 100-percent relative vapor pressure in the vapor phase. This phenomenon has been largely attributed to the fact that a 100-percent relative vapor pressure can hardly be attained experimentally and that the deviation is due to experimental error. Extrapolation of high relative vapor pressure values to 100 percent, however, still gives a considerable discrepancy. Sheppard and Newsome (*208*) have pointed out that most of the explanations offered are inadequate. They believe that additional surface is made available in the liquid phase as a result of the release of stresses which, in turn, result in the release of mutually satisfied hydroxyl groups.

Data of Koehler (*120*) on the swelling of green wood on heating in water at different temperatures can be explained in a similar way. He obtained an increase in external tangential dimensions and a decrease in radial dimensions with an increase in temperature which appears very much like the releasing of stresses. The tangential dimensionsi ncreased more than the radial were reduced, showing that the release of stresses must have caused a release of mutually satisfied hydroxyl groups with a resulting increased surface for sorption.

SORPTION BY "HYDRATE" CELLULOSE AND THE EFFECT OF BEATING

Sheppard and Newsome (*206*) have done considerable work on sorption by cellulose, its physical modifications, degradation products, and derivatives, using a vacuum method quite similar to that of Campbell and Pidgeon. "Oxycellulose" and "hydrocellulose" give slightly smaller moisture sorptions than the cellulose from which they were prepared, while "hydrate" cellulose obtained by previously treating with 20-percent sodium hydroxide, by regenerating from cuprammonium solution, and de-esterifying cellulose acetate all give increased moisture sorption over the whole relative vapor pressure range. Urquhart, Bostock, and Eckersall (*259*) have recently made similar observations. As was pointed out earlier, the "hydrate" celluloses give an expanded X-ray diagram, indicating that an intramicellar change has taken place. According to these data the change must result in an increase in the internal surface available for water.

Neale (*164*) and Sheppard and Newsome (*208*) have further shown that the accessible surface of a cellulosic material as indicated by the sorption does not seem to be related to the particle size as indicated by viscosity. Degradation of cellulose by acids or oxidizing agents (hydro and oxycellulose formation) greatly reduces the cuprammonium viscosity and the tensile strength and slightly reduces the adsorption power while mercerization affects the viscosity only slightly but increases the adsorption considerably. Degradation by acids and oxidizing agents evidently causes a nonreversible breaking down of the primary valence chains, thus greatly reducing the viscosity because of the shortened chains without appreciably affecting the adsorbing surface. On the other hand, mercerization has no effect on the chain length and hence practically none on the viscosity while it does cause either intramicellar swelling or a partially reversible separation of the hydroxy groups bound together by secondary valences that cannot be separated by water alone, thus accounting for an increased sorptive surface (p. 88).

The idea that beating a pulp causes an appreciable similar change has long been prevalent in the pulp and paper industry and is still strongly adhered to by Strachan (*242*, *243*). Campbell and Pidgeon (*38*), Seborg and the author (*201*), and Sheppard and Newsome (*208*) have, however, been unable to obtain significant differences in the sorptive power of beaten and unbeaten pulp. The author was also unable to obtain any significant difference in the moisture content-electrical conductivity relationship, using small pulp disks (*201*) and in the moisture content-adsorption compression relationship (*234*). Such results might be expected if beating caused hydration of the external surface of the pulp in the same sense that dissolving in cuprammonium solvent and regenerating increases the hydration of the whole bulk of pulp. For example, dissolving cellulose in cuprammonium solvent and regenerating increases the saturation-sorptive power from about 16 up to 23 percent. Only the external sorptive surface could be similarly affected by beating, that is, from 0.1 to 0.001 of the total sorptive surface. The increased sorptive power for the bulk of the pulp could only be from 4.4 to 0.044 percent.

It is true that all of these measurements give the moisture held under finite reduced activity condition. There may be considerable difference in the amount of moisture held by an infinitesimal attractive force. It is inconceivable, however, that this loosely held water or the relatively small increase in more firmly held water just considered can affect fiber-bonding properties. It thus appears that the strength of a sheet is increased by beating of the stock not because of any increased hydration effect, but because of defibrillation, which increases the external bonding surface and the possible formation of a dextrinlike bonding material on the surface as postulated by Bell (*24*). Then, too, the surface tension effects considered by Campbell (*37*) play their part. These will be considered further under the heading of Swelling. Campbell (*37*) and Cottrall (*45*) have so adequately discussed the so-called "hydration" of pulp in recent articles that no attempt will be made to go into the subject more fully here.

WAYS IN WHICH WATER IS HELD

Water is held by cellulosic materials in three distinct ways, namely, as water of constitution, as surface-bound or surface-adsorbed water, and as capillary condensed water. Other means of binding water, such as by solid solution, have been suggested. They tend to overlap with the foregoing classifications and, as they are incapable of experimental differentiation they have little practical value.

The line of demarcation between the water of constitution and surface-bound water is by no means sharp. Surface-bound water may be held so tenaciously that even under a high vacuum such high temperatures have to be used for its removal that decomposition of the material will result. In the case of cellulosic materials the cellulose is definitely changed when dried for prolonged periods at temperatures only slightly above the normal drying temperatures of 105° to 110° C. Undoubtedly, some of the bound water remains fixed on the fibers at this temperature even under a high vacuum. For this reason bound water and total sorption determinations on cellulosic materials are dependent upon the arbitrary dry weight used which varies somewhat with the method of drying. Bateman and Beglinger (*18*) determined the moisture content of wood by drying it in an oven under different conditions and distilling with water-insoluble organic liquids. Drying for 24 hours at 105° over phosphorous pentoxide removed 0.2 percent more water than drying without phosphorous pentoxide, but after 7 days the difference was only about 0.02 percent. Drying at 105° under a pressure of 55 mm. of mercury removed 0.3 percent less moisture in 24 hours and 0.4 percent less in 7 days than drying at atmospheric pressure over phosphorous pentoxide. Distilling in toluene and xylene (boiling points 111° and 140°) for 1 to 4 hours gave practically the same moisture-content values as were obtained by drying in an oven over phosphorous pentoxide for 5 to 7 days. Distilling in eucalyptus oil (boiling point 171°) increased the moisture evolved by only 0.3 percent. Distilling in tetraline (boiling point 207°) increased the moisture evolved by 4.15 percent, showing that destructive distillation had become appreciable. The efficient heat transfer in the distillation method thus makes it possible to remove moisture much more rapidly than in drying in an oven and makes possible the use of higher temperatures. Even when the temperature is raised 70° above the boiling point of water only 0.3 percent more moisture is lost than in drying in an oven to constant weight. From this it appears that the bound water retained under normal drying practice is probably less than 1 percent.

The transition between surface-bound water and water held by capillary forces also appears to be gradual. All the available data on sorption by cellulosic materials give smooth sigmoid moisture content-relative vapor-pressure curves in which the increase in moisture content per unit change in relative vapor pressure decreases to a minimum at a relative vapor pressure of about 0.30 to 0.50, and then increases to a maximum at the fiber-saturation point. The inflection point is generally believed to indicate the transition point between the true surface adsorbed or bound water and capillary condensed water. This supposition is supported by the fact that calculations of the pore size from the equilibrium relative vapor pressure at the inflection point, using Kelvin's equation (6), give values of r only a few times the molecular diameters. Water at a relative vapor pressure of 30 percent at room temperature gives a value of r of 8.7 A which is only 2.3 times the molecular diameter. This is very near the limiting distance of primary molecular attraction and would be expected to represent the limit of applicability of Kelvin's equation.

The fact that the transition between the bound water and water held by Capillary forces is not abrupt indicates that the points of adsorption must vary in activity as in the case of a metal catalyst. The attractive force at the weakest of these adsorption points must be of the same order of magnitude as the capillary force exerted in the finest capillary. Peirce (*177*) in his two-phase theory of adsorption, instead of picturing a gradual transition between bound water and water held by the capillary forces, with perhaps a slight overlapping, pictures a dynamic equilibrium between the two ways in which water is held. In this theory the fraction of the total water taken up that goes into the bound phase is proportional to the ratio of unoccupied true adsorption positions to the total number of adsorption positions. Not only elastic gels, such as all cellulosic materials, but also such simple liquid mixture systems as sulphuric acid and water give the smooth sigmoid moisture content-relative vapor-pressure curves (*110*). A more intimate study of the latter may prove of value in definitely explaining the nature of sorption by cellulosic materials.

If the inflection point in the moisture content-relative vapor-pressure curve does represent the limit of truly bound water, then the moisture bound by various cellulosic materials should vary between 4 and 10 percent at room temperatures. Similar values are predicted by Sheppard from the following considerations (*204*). Considering the seat of true surface adsorption, the hydroxyl group of the amylene oxide linkage of the cellulose structural units with each of the hydroxyls available for the sorption of 1 molecule of water, cellulose could take up 33 percent of water. "Hydrate" cellulose, however, takes up only 23 percent and native cellulose only 16 percent at saturation (*206*). The continuous curvature of the adsorption curves just considered and the differential heat of wetting curves furthermore indicate that part of the water must be held by a much weaker force than the water directly bound to the free hydroxyl groups. X-ray evidence points to the fact that the adsorption is intermicellar rather than intramicellar. On the basis of the size of the X-ray micellar units only about half of the hydroxyl groups would be on the surface. All of these can hardly be available for water sorption for if they were, cellulose would be peptized in water. Sheppard thus believes that not much more than 5 percent of water can be held by primary sorption to hydroxyls in the case of native cellulose, nor more than 7 percent in the case of "hydrate" cellulose.

The author and Hansen (*232*) have recently shown, in connection with replacement studies (p. 58), that the last 5 to 6 percent of a swelling liquid cannot be replaced in wood by a nonswelling liquid without shrinkage occurring. Although the surface-bound water can be replaced by another swelling liquid having an affinity for the wood, it cannot be replaced by a nonswelling liquid that has no affinity for the wood. The fractional part of the total possible volumetric shrinkage which occurs on replacing a swelling liquid in the fiber structure with a nonswelling liquid thus appears to be a measure of the fractional part of the sorbed swelling liquid which is bound by the surface.

There are a number of methods for determining the transition between the water held by capillary forces and the free bulk water, the point below which the activity of the water becomes less than unity. This point has been designated by the Forest Products Laboratory as the "fiber-saturation point." It can be obtained by extrapolating the moisture content-relative vapor-pressure curves to a relative vapor pressure of unity.

Extrapolation of desorption and adsorption curves to unit relative vapor pressure, however, gives somewhat different values, the former being higher than the latter. This can be explained on the basis of Urquhart and Williams' theory of the availability of the hydroxyl groups. The fiber-saturation point will thus vary somewhat with the condition of the fibrous material. Under similar previous treating conditions, however, surprisingly good agreement for the fiber-saturation point of wood and sulphite pulp were obtained by the author by six entirely different methods; namely, from the variations of relative vapor pressure, shrinkage, strength, electrical conductivity, heat of wetting (calculated and measured), and adsorption compression with a decrease in the moisture content (p. 89). The shrinkage method seems to be applicable only in the case of a coherent material like wood and not in the case of a matlike paper because the drawing together of the fibers of the latter on drying cannot be distinguished from the true shrinkage of the fibers themselves. The measurements might, however, be made microscopically on a single fiber. Wood, as will be shown later, does not shrink until the moisture content falls below the fiber-saturation point and then the shrinkage progresses linearly with a decrease in moisture content. The measurement can be made with accuracy only on very thin cross sections of less than a fiber length in thickness so as to eliminate almost completely the drying moisture gradients. This is essential, as part of the wood would otherwise dry to the fiber-saturation point and start to shrink, while the average moisture content was still above the fiber-saturation point (*230*). The presence of appreciable gradients will also change the normal relationship between external and internal volume changes as will be shown later. When these gradient effects are properly eliminated, the objections to the method raised by Barkas (*12*) are practically eliminated. The strength of a fibrous material, as was shown under the heading of Mechanical Properties, increases as the separation of the micelles decreases; that is, the strength and the shrinkage are parallel properties. The strength measurements, as a result of the complexity of the phenomena, and the fact that separate specimens are necessary for each test, can, however, hardly be expected to give more than the correct order of magnitude for the fiber-saturation point (*251*, *279*). The electrical conductivity method depends upon the fact that the conductivity changes at a very great rate with changes in moisture content below the fiber-saturation point, whereas the change above is relatively small, as was shown under the heading of Electrical Conductivity. This method, like the shrinkage method, depends upon the absence of moisture gradients in order to obtain accurate results. It is applicable to pulp mats as well as to wood. It is the simplest of all the methods from an experimental standpoint and the reproducibility of results is good (*219*). The heat of wetting (*233*) and the absorption compression (*234*) methods are more of theoretical than of practical interest because of the more difficult experimental technic involved. Both of these methods depend upon the fact that upon addition of water above the fiber-saturation point heat is not evolved and water is not compressed.

The fiber-saturation points obtained by these different methods are in good agreement. For spruce wood the variation is not greater than 1 percent. The fiber-saturation point changes with changes in temperature. It is increased approximately 0.1 percent for each degree centigrade lowering of the temperature (*233*). Most woods, according to data of the author, have fiber-saturation points ranging from 27 to 31 percent at room temperature. Grace and Maass [10] give values ranging from 21 to 31 percent from sorption data on wood. Kapur and Narayanamurti (*109*) give values for the fiber-saturation point of different tree barks from sorption measurements ranging from 22 to 30 percent. Wood pulps and isolated lignin have similar fiber-saturation points. Bleached pulps, alpha cellulose, and cotton linters have somewhat lower fiber-saturation points, values as low as 15 percent having been reported. Oguri and Nara (*169*) determined the fiber-saturation points of a number of cellulosic materials at two temperatures. Standard cotton, alpha pulp, and alpha cellulose from bamboo gave 16.8, 23.3, and 26.0 percent at 20° C., respectively. They gave 15.2, 18.0, and 25.8 percent at 30°, respectively. Nitrocellulose gave a value of only 6.7 percent at 20°. Rayons, other than the acetate, have been shown by Urquhart and Eckersall (*261*) to have somewhat higher fiber-saturation points as a result of the "activation" treatment. Viscose rayons gave values ranging from 33 to 45 percent at 25°. Cellophane gave 33 percent, Lilienfeld viscose rayons gave 35 to 39 percent, and cuprammonium rayons gave 35 to 41 percent. Acetate rayon, on the other hand, gave only 18 percent (p. 88).

The freezing method has been used by a number of investigators (*31*, *102*, *171*) to determine the so-called "bound water" or fiber-saturation point in a number of different plant materials. Two major difficulties are involved in the interpretation of the data: (1) The supercooling of finely dispersed water may be very appreciable, and (2) the freezing at lower temperatures involves a reduced activity of the unfrozen water (*31*). Kistler [11] has recently shown that emulsions of water in oil can be supercooled to temperatures as low as −50° to −60° C. without completely freezing. These droplets are further of a size that would only slightly reduce the vapor pressure and the freezing point. Freezing measurements will therefore give the fiber-saturation point only in the case where all the free water is frozen.

R. Seborg and the author made some preliminary measurements upon the freezing of water in wood, using the dilatometer method of Jones and Gortner (*102*). Extrapolation of the line for the frozen system back to 0° C. to correct for reduced activity gave fiber-saturation points of about 42 percent, whereas the values obtained by the previously described methods at 0° are about 32 percent. It thus appears that the water corresponding to the difference between these two values did not freeze, although it appears to be free water. This result is, of course, to be expected on the basis of Kistler's experiment. All of the freezing did not occur at one temperature as in the investigations of Jones and Gortner (*102*) on gelatin and egg albumin, but some freezing occurred down to −25° or lower, as in Foote and Saxton's (*66*) measurements, even though the temperatures were held sufficiently long to attain equilibrium. The unfrozen water at decreased activities corresponding to different decreased temperatures showed a constant ratio to the desorption moisture contents at the same activities. Evidently the free water, which showed no tendency to freeze at −4° to −5°, still showed no tendency to freeze at −25° because of the lack of nuclei to start freezing. The method thus appears to be unsatisfactory for determining the fiber-saturation point of wood. This lack of sufficient nuclei to cause complete freezing of free water may, of course, vary with different materials. The method should in any case be used with caution.

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[10] GRACE, N. H., and MAASS, O. THE SORPTION OF WATER VAPOUR IN VARIOUS CANADIAN WOODS. Quart. Rev. Pulp and Paper Lab. Forest Prod. Lab. Canada 5 (pt. 1, Jan.–Apr.): 2–26. 1931. [Mimeographed.]

[11] KISTLER, S. S., LIEB, W. E., DRUMMOND, J. E., and FREEMAN, I. R. UNDERCOOLING OF WATER AND ITS POSSIBLE SIGNIFICANCE IN THE MEASUREMENT OF BOUND WATER. Paper presented at meeting of colloid division, Amer. Chem. Soc., New York. 1935. (Unpublished. Title in program.)

"Bound-water" measurements have also been made by determining what portion of the water does not act as a solvent for a material like sugar. In some cases the equilibrium sugar concentration was determined by a freezing method (*167*). These measurements are subject to the same criticisms as the foregoing freezing method. In other cases, such as in the measurements of Barkas (*11*) on wood, the concentration measurements were made interferometrically. Barkas found that dry Sitka spruce took up approximately 20 percent of water from 10- to 30-percent sugar solutions. He thus considers the fiber-saturation point to be 20 percent. The sugar should affect the wood-water equilibrium in the same way that the author has shown salts to affect the wood-water equilibrium (*229*). The wood should be in equilibrium with a reduced water activity equal to the relative vapor pressure of the sugar solution. The "bound water" plus the capillary water will thus be appreciably less than the fiber-saturation point. Barkas' results thus indicate that practically all the sorbed water is surface-bound water. This is contrary to the evidence just given (p. 45) and no positive explanation is at present available.

SORPTION OF NONAQUEOUS VAPORS

Sheppard and Newsome (*207*) have determined the sorption at saturation pressures of the normal aliphatic alcohols by cotton linters. The cotton linters show a linear decrease in the sorption from the saturated vapor in going from water to n-butyl alcohol. The sorption values at 30° C. are 15 percent for water, 11.2 percent for methyl alcohol, 8.6 percent for ethyl alcohol, 5 percent for propyl alcohol, and 1.5 percent for butyl alcohol. A similar decrease in the swelling of wood was obtained by the author (*230*) for the same series of alcohols. Sheppard and Newsome determined the sorption over the complete relative vapor-pressure range only for ethyl alcohol sorbed by cellulose acetate. The typical sigmoid sorption curve was obtained.

Campbell (*37*) determined the sorption of methyl alcohol by several different pulps. The first adsorption was carried to a relative vapor pressure of 50 percent and the samples were then subjected to a high vacuum for a week, but still 0.75 percent of alcohol remained in the ground wood and over 2 percent in the pulps. Subsequent adsorptions gave normal sorption curves and hysteresis. The saturation sorption of cellulose for the methyl alcohol is slightly less than for water but its retention for methyl alcohol at low relative vapor pressure is greater.

Grace and Maass (*73*) determined the sorption of amylene, ethyl ether, and methyl alcohol on white spruce wood. Amylene was sorbed to the extent of 0.5 percent at 25 cm of mercury pressure. No increase in sorption resulted when the pressure was increased to the saturation pressure. The sorption of ether was 0.5 and 1.2 percent, respectively, at 10.2 and 38.2 cm of mercury pressure. The ether was readily and completely removed on evacuation. The sorption of methyl alcohol was rather large, 6.4 percent at 34.4 percent relative vapor pressure and 11.7 percent at 83.1 percent relative vapor pressure. A pronounced sorption hysteresis was also observed (p. 87).

Wiertelak and Garbaczówna (*275*) have shown that sorbed alcohols are partially retained by cellulose, even on oven drying to constant weight at 105° C. Various forms of cellulose retained from 1.5 to 2.2 percent of ethyl alcohol. Cotton retained 0.8 percent of methyl alcohol, 1.6 of ethyl alcohol, 2.6 of propyl alcohol, and 1.7 percent of n-butyl alcohol. The retention of diethyl ether, benzene, and gasoline was negligible. The sorbed alcohols could, in all cases, be removed by washing with ether or water.

Sheppard and Newsome (*207*) have pointed out that the rate of sorption of water vapor is but slightly affected by the structure of the adsorbent while the rate of sorption of alcohols is appreciably affected by the structure of the adsorbent. This can be explained on the basis of the small water molecule, which causes a rather large swelling of the fibrous material, being relatively unhindered in diffusion while the larger alcohol molecules, which cause considerably less swelling, are quite appreciably retarded in diffusion. They suggest that sorption measurements with various organic molecules may furnish a valuable means of studying capillary structure of cellulosic materials.

SWELLING

NATURE OF SWELLING

There are three essential characteristics of the phenomenon of swelling, all of which were recognized as early as 1858 by Nägeli (*161*): (1) That the solid material increases in both dimensions and weight with an accompanying thermal change as a result of the taking up of another phase, (2) that the combined phases become and remain homogeneous in a microscopic sense, and (3) that the cohesion of the solid is reduced but not eliminated. The phenomenon of swelling is characteristic of all elastic colloidal materials but differs somewhat for different types of materials. Gelatin, for example, can swell to the point where the cohesion of the solid becomes negligible; that is, it shows a gradual transition from a swollen to a dispersed condition. Cellulosic materials, on the other hand, show no such property in ordinary swelling agents. The cohesion of the solid structure is under practically all conditions sufficiently great to limit the distention of the solid and imbibing of liquids. Natural cellulosic materials also show a definitely oriented structure which gives rise to differences in the dimensional swelling in the three structural directions. Cellulosic materials differ from gelatin still further in that they exhibit a coarse capillary structure that is capable of taking up liquids without accompanying swelling as well as the characteristic capillary structure of swelling. This fact greatly complicates the measurement of the swelling of cellulosic materials. The swelling of gelatin can be followed by weight changes alone. This can be done in the case of cellulosic materials only under conditions that make it possible to distinguish adsorption from absorption. For example, a piece of wood can take up about 30 percent of water on the basis of the weight of the dry wood with accompanying swelling. When immersed in water it may take up from 150 to 300 percent more water in the coarse capillary structure without any further swelling taking place. So-called swelling measurements have been made on cellulosic materials by determining the increase in weight of the material after immersion in various liquids and solutions. This, however, gives a measure of the absorbancy which depends upon the capillary structure of the material, the surface tension of the liquid, and its ability to wet the solid, as well as on the extent of swelling. It would hence be preferable to make swelling measurements of cellulosic materials on a volume-change basis. This, however, is difficult if not impossible to do experimentally because of the internal as well as external dimensional changes. Even in wood where the external dimensional changes are easy to determine, the internal changes in the fiber lumen may be very complicated, thus making possible only approximations of the magnitudes of the changes.

Then, too, it is difficult to distinguish between true shrinking and swelling of the fibers themselves and the dispersion of the fibers. This is especially true in the case of paper. Campbell (*37*) has shown that in the formation of a sheet the initial shrinkage is due to the drawing together of the fibers as a result of the surface-tension forces. At first the force is such as to draw the fibers down to the screen and later to draw them together as the water is then held between the fibers in layers bounded by concave surfaces which extend in the direction of the fiber axis. The pull between the fibers is equal to twice the surface tension of water. The fibers will thus be drawn together until the resisting structural force is equal to twice this surface tension. As Campbell has shown, the effective tension force per unit of area will be vastly greater for fibrils and broken-down fibers than for intact fibers. Hence a sheet made from a beaten pulp shrinks on formation considerably more than an unbeaten pulp, thus resulting in a denser sheet. As was shown under the heading of Mechanical Properties, the strength of a sheet of paper is largely dependent upon its density. Doughty (*49*) showed that the formation of sheets from unbeaten pulp under pressures that produced sheets of the same density as those obtained from beaten pulp without applied pressure gave sheets of practically the same strength. Beating a pulp thus serves as a substitute for the application of large external pressures in the formation of a sheet.

Two different shrinkages are thus effective in the formation of a sheet of paper: (1) The drawing together of the structural units followed by (2) a shrinkage of the structural units themselves. It will be shown later that the shrinkage of the fibers themselves very likely involves the same type of surface tension forces, but on account of the reduced magnitude of the films of water in the capillary structure, the forces per unit area will be vastly greater than those just considered. This latter shrinkage is quite reversible, whereas the former may be only partially so. The shrinkage of the fibers also involves appreciable vapor-pressure lowering whereas the drawing together of the fibers does not.

VOLUMETRIC SHRINKING AND SWELLING OF WOOD

Wood is an ideal material with which to study the volumetric swelling of a fibrous structure as it is practically free from the effect of drawing together of structural units. It is also easy to determine the over-all external dimension changes of wood. The shrinking and swelling of wood will hence be considered more critically than that of other cellulosic materials.

A recent publication by the author (*230*) shows that the external dimensional swelling of small sections of wood is a direct function of the moisture content practically up to an activity of unity. Mörath reports similar observations (*155*). This linear relationship might be expected to hold on a total shrinkage basis over the sorption range, if the effect of adsorption compression is small. The fact that it holds for shrinkage manifested externally indicates that internal shrinkage in the grosser capillary structure must be proportional to the external change or practically negligible.

The internal dimensions of the voids in a hypothetical gel, free from stresses and dried under stress-free conditions, would change the same as the dimensions of the bulk of gel that would just fill the voids. Under these conditions swelling and shrinking as transmitted to the external dimensions would be independent of the bulk density or degree of porosity of the gel. This is not the case for wood which shows an appreciably greater swelling and shrinking for a greater density (*166*), indicating that the external swelling is not independent of the volume of the voids. The increase in the volume of the voids on swelling is thus necessarily less than that for the same volume of gel; in fact, the voids may not increase in size at all or may even decrease during the course of swelling. This is perhaps to be expected on the basis of the structure of wood fibers, which are made up of bundles of fibrils approximately parallel to the length of the fiber with outer fibril wrappings at right angles. External dimension changes are easily restrained because of the structure, thus necessitating compensating internal changes in order that equilibrium may be attained.

The volumetric shrinkage of small sections of wood dried under minimum stress conditions is approximately proportional to the bulk density of the sections with but slight shifts of the proportionality constant for different species. The proportionality constant is practically equal to the fiber-saturation point. As a first approximation the relationship

$$S_e=\rho_w f_s \tag{19}$$

seems to hold, where S_e is the percentage volumetric shrinkage from the saturated to the oven-dry condition on an external dimension change basis, ρ_w is the bulk density of the wood on a dry weight-green volume basis, and f_s is the fiber-saturation point expressed in terms of the volume of water held per 100 g of dry wood. The relationship requires that the volume of the grosser capillaries does not change with changes in moisture content and that the total volumetric swelling is approximately equal to the volume of water taken up (*230*).

Schwalbe and Beiser (*197*) find from an analysis of their data for the swelling of wood that the fiber-cavity dimensions are practically unchanged when assuming a fiber-saturation point of their wood of 30 percent. Beiser (*23*) has also shown from microscopical studies of wood cross sections that the change in the size of the fiber cavities resulting from shrinking and swelling of the wood is small. He found that the fiber cavities of spring wood increase in diameter slightly or do not change at all upon swelling of the wood, while the fiber cavities of the summer wood actually decrease slightly in size. Such an effect would be expected as the heavier walled, denser summer-wood fibers would tend to exhibit a greater external swelling than the less dense spring-wood fibers. The summer-wood fibers would thus exert an external tension on the spring-wood fibers and the spring-wood fibers would exert an external compressive force on the summer wood. The tension would tend to cause a greater external swelling of the spring wood than normal and hence a compensating increase in the size of the fiber cavity; whereas the external compression on the summer-wood fibers would tend to reduce their external swelling. This would have to be compensated for by a swelling into the fiber cavities, resulting in a decrease in their dimensions. The author (*231*) has also obtained data on the permeability of the fiber cavities of wood to air of different relative humidities that indicates that the size of the cavities change but slightly with swelling and shrinking of the wood. The evidence thus strongly indicates that the change in volume on swelling is approximately equal to the volume of water taken up.

Collins (*44*) was able to show by microscopically following the change in cross-sectional area of cotton fibers with changes in relative vapor pressure, that the swelling parallels the sorption of water vapor. Variations of swelling in water with changes in temperature also parallel the changes in sorption with temperature. Using the same material for which Urquhart and Williams (*257*, *262*, *263*, *264*, *265*) obtained a fiber-saturation point of about 31 percent, Collins found an average cross-sectional swelling of 43.9 and a longitudinal swelling of 1.12 percent. Assuming that the increase in volume is equal to the volume of water sorbed, he calculated the apparent specific volume of water to be between 0.8 and 0.96, using Davidson's (*47*) value 0.647 for the specific volume of the cotton. Because of the variations in the experimental data no definite conclusions can be drawn regarding the validity of the assumption. It is safe to say, however, that the increase in volume on swelling is of the same order as the volume of water taken up. Single cotton fibers thus appear to be similar to wood in this respect.

An extreme case in which the normal external swelling of wood can be shifted to an internal swelling has been demonstrated by Tiemann (*252*). A dry block of wood is clamped in a mechanical device so that its external dimensions cannot change. It is then placed in a saturated atmosphere or in water and allowed to come to equilibrium. When removed from the clamp and dried, the external dimensional shrinkage is practically the same as if the block had previously swollen normally. The block can again be placed in the clamps and the procedure repeated. After 10 such cycles Tiemann obtained a reduction of the volume of the block to two-thirds of its original value. Although the dimensional swelling can be shifted under stress the volumetric swelling is apparently unaltered.

DIRECTIONAL SHRINKING AND SWELLING

Although simplifying generalizations can be made regarding the volumetric swelling under special conditions, they cannot be made in the case of directional swelling, which is greatly complicated by the nature of the fibrous structure. The directional swelling of bundles of fibers, mats of fibers, and films of fibers depends upon the orientation of the fibrils within the fibers as well as upon the orientation of the fibers themselves, their bonding, and the stresses set up on drying or soaking. Because of the complexity of the phenomenon, the effects of the different variables on the dimensional swelling of such materials have received practically no theoretical consideration. The effect of changing manufacturing variables can be interpreted in terms of dimensional changes in swelling even qualitatively only insofar as the effects of these variables upon orientation, bonding, and stresses are known. The case is but slightly simpler for wood. The angle that the fibrils make with the axis of the fibers is known to vary considerably among species and for fibers taken from different parts of the tree. Compression wood shows a poorer axial orientation of the fibrils (*213*) than normal wood. The thickness of the cell wall, which varies with seasonal growth conditions, affects the density of the wood and the subsequent dimensional swelling and shrinking as was previously shown. The proportion and arrangement of the different types of structural elements, such as fibers, pores, resin ducts, and rays, also affects directional swelling. Then, too, the lignin-cementing material, the hemicelluloses, and extractives may play their part. For this reason only a few generalizations can be made regarding the directional swelling of wood. In general, the external swelling in the tangential direction varies from 5 to 12 percent, in the radial direction from 2.0 to 7.0 percent, and in the longitudinal direction it is a small fraction of 1 percent. The slight longitudinal swelling is due to the fact that the greater mass of the fibrous structure is oriented longitudinally. The difference between the tangential and the radial swelling is accounted for on the basis of the ray cells, which have their longitudinal component in the radial direction, restraining the normal dimension changes in that direction.

In large wood specimens appreciable moisture gradients are set up during the process of drying or soaking that complicate the directional shrinking and swelling. The surface always dries below the fiber-saturation point before the inner part of the wood reaches this stage, thus causing stresses to be set up which may result in surface checking. If the surface can withstand this stress, it sets in tension and when the center finally dries and tries to shrink stresses are again set up that may result in honeycombing. Under these conditions external shrinkage is reduced below normal, thus necessitating a compensating internal change. This would naturally cause deviations from the ideal shrinkage-fiber-saturation point relationship (*230*).

The various directional swelling factors just given show their effect in the changes in the size of the different parts of the capillary structure of wood. As was previously shown (p. 54), the fiber cavities change but slightly in cross section on normal shrinking and swelling of wood in water. The author (*231*) has shown, however, that the pit-membrane pore radii increase in size on the shrinking of the wood by as much as 10 percent. Evidently the thin pit-membrane pores respond to relative vapor pressure changes more rapidly than do the thicker cell walls. As the rim of the pit membrane is thus restricted in its shrinkage, the shrinking will have to occur internally rather than externally, thus resulting in an increase in size of the pores.

SWELLING IN AQUEOUS SOLUTIONS

In certain concentrated aqueous solutions cellulosic materials swell beyond the normal water-swollen dimensions. Saturated electrolyte solutions that tend to disperse cellulose at higher temperatures cause such increased swelling at lower temperatures (*86*). The order of swelling power of the salts follows the well-known lyotropic series, the more hydrated ions being the most effective swelling agents. The author (*229*) determined the external volumetric swelling of wood in saturated solutions of a series of chloride and a series of potassium salts. The decreasing order of swelling is as follows:

$$\mathrm{Zn > Li > Ca > Mg > Mn > Ba > Na > NH_4 > K}$$
$$\mathrm{CNS > I > CrO_4 > Br > Cl > NO_3 > SO_4 > ClO_3}$$

This is practically identical to the order of decreasing solubility in mole equivalents per liter of the salts, decreasing partial specific volume occupied by the salt in solution, decreasing surface tension of the salt solutions, and increasing relative vapor pressure of water over the solutions. The investigation also showed that the sorbed water attains a salt concentration practically the same as in the bulk solution, indicating that the water held below the fiber-saturation point takes up salt. The Donnan equilibrium effect in this case would be negligible, not only because of the extremely low ionization constant of the cellulose (*163*), but also on account of the high salt concentration. The salt, in being taken up by the fine structure, displaces part of the sorbed water but less than the volume of salt taken up. From this it follows naturally that swelling should be greatest with the salts having the greatest partial specific volume in their saturated solutions.

When wood that has been swollen in saturated salt solutions is dried, shrinkage does not occur until the relative humidity under which the drying takes place becomes less than the relative vapor pressure in equilibrium with the saturated salt solutions. The shrinkage of wood to the oven-dry condition is also retarded by an amount equal to the volume occupied by the salt deposited from solution in the swelling structure (*229*).

Cellulosic materials swell appreciably in strong alkalies but not in dilute mineral acids. In spite of this the pH of a salt seems to have a negligible effect upon its capacity to cause swelling (*229*).

Kanamaru (*106*) has determined the effect of the hydrogen-ion concentration on the so-called swelling of cellophane sheets. His measurements were made on a weight-change basis so that they are really measurements of imbibition. A minimum in the so-called swelling occurred at a pH of about 6.7 and maxima at about 5.7 and 8.5. Another minimum occurred at a pH of 11.5 followed by a rather large swelling. In the case of wood no such pH effect is obtained when the actual external dimension volumetric swelling is measured. The author found no deviation from the normal water-swollen condition up to a pH of 8. A gradually increasing swelling occurred from here becoming very large at high pH values. The difference between these two results hardly seems due to the fact that wood contains other materials than cellulose, as the swelling of wood and the sorption of cotton have been shown to be quite parallel (*230*). The difference must be that Kanamaru's measurements involve the mechanical imbibing of solution which manifests itself only partially as a true swelling. The increased imbibition on the addition of both acids and bases may very well be due to a combination of surface tension and ζ potential effects. The fact that the weight increases obtained by Kanamaru considerably exceed the true sorption by cellophane (p. 88) also points to an imbibition effect. The same imbibition effects enter into the measurements made by Schwalbe and Fischer (*198*) of the so-called swelling of paper in dilute electrolyte solutions. They obtained, in general, slightly reduced imbibitions with acids and slightly increased imbibitions with alkalies and with salts. So-called swelling measurements by the sedimentation volume method of Schwalbe and Beiser (*197*) also give imbibition values. The presence of electrolytes in general increases the imbibition of solution. The imbibition varies with the previous history of the material.

Katz (*114*) has shown that not only electrolytes in concentrated solution cause swelling of cellulosic materials beyond the water-swollen dimensions, but also a considerable number of nondissociated organic substances, such as thiourea, chloralhydrate, resorcinol, and benzene sulphonates. Katz found that all organic compounds containing nonoxidized sulphur are effective as swelling agents in aqueous solution. The presence of halogens also causes swelling, the iodides being more effective than the bromides, and the bromides more effective than the chlorides. The sulphur and halogen groups he believes are bound by the free hydroxyl groups of the cellulose micelles and other polar groups of the molecules, in turn, bind water, thus accounting for the swelling.

Swelling agents that cause an appreciable swelling beyond the normal water-swollen dimensions further complicate the directional swelling. It has been observed that isolated fibers actually shorten when swollen in strong swelling agents, such as aqueous alkali solutions. Katz (*114*) suggests that this may be due to loosening of the micellar structure, the micellar threads tending to bend or aline themselves spirally, or that each micellar crystallite is enclosed in a nonswelling membrane which upon swelling of the contents tends to become spherical, whereby the fiber becomes shorter (*139*). Ritter (*189*, *190*) has observed that wood fibers, when swollen in strong alkali solutions that cause swelling beyond the normal water-swollen dimensions, swell internally to almost completely fill the lumen. This he has shown to be due to the resistance to external swelling beyond the normal water-swollen dimensions caused by the fibril wrappings about the fibers at right angles to their length. If these wrappings become broken a large external swelling results. Ritter thus does not consider it necessary to postulate the existence of a hypothetical nonswelling membrane surrounding each of the structural units, as Lüdtke has done. The restrained and distorted dimensional swelling can be explained in every case entirely on the basis of variations in orientation of the structural units.

Saitō (*193*, *194*) has critically studied the cross-sectional swelling of various cellulose fibers in sodium hydroxide solutions varying in concentration from 0 to 50 percent. The cross section of the fibers becomes more circular on swelling. Alcohol-benzene extracted cotton shows a maximum swelling in 20- to 25-percent sodium hydroxide solutions at 25° C. Purified cotton shows a maximum swelling at lower concentrations, namely, 13 to 15 percent. When the temperature is decreased the cross-sectional swelling of the fibers is increased at a given alkali concentration, and the maximum swelling point shifts to lower alkali concentrations. The cross-sectional swelling in concentrated alkali solutions is not reversible. No definite relationship between the cross-sectional swelling and X-ray swelling diagrams was obtained.

SWELLING THEORIES

A great many attempts have been made to explain theoretically the reason for the taking up of a swelling medium by a swelling solid. Three different mechanisms have been suggested. Pauli and Handovsky (*173*, *174*) believe that the adsorbed ions together with the oppositely charged ions, which in order to maintain electrical neutrality become immobilized, in close proximity to the adsorbed ions, bring their sphere of water with them, and that this water of hydration of the ions is responsible for swelling. Tolman and Stearn (*253*), Bovard (*27*), and Gasell and Minor (*71*) believe that the electrical charge set up on the surface as a result of selective adsorption of ions or molecules (p. 34) results in a repulsion of the like surface charges that allows water to enter mechanically. Proctor and Wilson (*185*) believe that swelling is due to the setting up of a Donnan membrane equilibrium that results in a higher concentration of ions within the membrane than on the outside and a subsequent taking up of water by osmosis because of the concentration difference. The first theory is applicable for aqueous swelling agents but it is difficult to apply for nondissociated organic swelling agents. The second theory is applicable for water and dilute aqueous solutions, but in concentrated aqueous solutions of electrolytes the ζ potential as previously shown becomes zero and consequently it is hard to conceive of an electrostatic repulsion on the surface of the cellulosic material. It is more applicable, however, in explaining the swelling in nondissociated organic liquids than the first theory. The third theory requires the presence of diffusible electrolytes in solution and an appreciable ionization constant of the swelling material to be applicable. The ionization constant of cellulose has already been pointed out to be very small. Even if it were appreciable it would become ineffective in concentrated electrolyte solutions. It thus appears that none of the theories are generally applicable to explain all forms of swelling.

The author (*230*) has explained the swelling beyond the normal water-swollen dimensions in concentrated solutions on the basis of a combined sorption-solution pressure-structural resistance equilibrium. It was previously shown under the heading Swelling in Aqueous Solutions that the swelling of wood beyond the water-swollen dimensions in saturated salt solutions increases with an increase in the partial specific volume of the salt in solution. The swelling in all cases is less than the volume of salt taken up, indicating that some water is displaced. Salt is at first taken up without any appreciable swelling occurring. Both the solution pressure of the salt and the structural resistance of the wood exceed the force with which the last few increments of water are held by the wood. Hence, water is displaced. As more salt enters the swelling structure more water has to be displaced or the material has to swell. The further removal of water requires a greater and greater force. This soon exceeds the structural-resistance force so that swelling rather than water displacement results. The solution pressure of all appreciably soluble salts is the predominating force and hence becomes satisfied by the attainment of practically the same concentration within the swelling structure as on the outside. This is done at first at the expense of the sorbed water and later at the expense of the structural resistance of the material. The greater the partial specific volume of the salt in solution the greater will be the resultant increase in the volume of the material necessary for the attainment of equilibrium. This mechanism it seems would also explain the swelling of cellulose in concentrated aqueous solutions of organic materials described by Katz (*114*).

SWELLING IN ORGANIC LIQUIDS AND THE REPLACEMENT PROCESS

The swelling of cellulosic materials in dry organic liquids is, in general, less than in water, decreasing with a decrease in the polarity of the liquid. The swelling in nonpolar hydrocarbons and in benzene is negligible. A series of measurements by R. C. Rounds and the author (*230*) on the swelling of oven-dry wood in dry organic solvents showed that formamide and formic acid caused a greater swelling than did water. A series of normal alcohols from methyl to butyl alcohol gave a decreased swelling with an increase in molecular weight, the butyl alcohol causing only a slight swelling. This is in agreement with Sheppard and Newsome's (*207*) sorption measurements. A series of fatty acids gave a similar decrease in swelling with an increase in molecular weight except that the decrease per CH_2 group added was less than for the alcohols. A series of benzene derivatives gave an increasing swelling in the order $H < CH_3 < NH_2 < CHO < Br < Cl < NO_2$. This is the same order as that of the increasing dipole moments of the liquids (*230*) (p. 89).

Swelling in solutions of nonelectrolytes and in pure organic liquids cannot be accounted for by Pauli's theory because of the absence of ions. Surface adsorption of solvated molecules may, of course, take place, but how the large molecules can penetrate the nonswollen structure without postulating the preexistence of appreciably sized capillaries is difficult to explain. The electrical repulsion theory is more applicable. A ζ potential is set up on the surface as a result of molecular adsorption, both in the case of aqueous solutions and pure organic liquids. This causes a repulsion of primary valence chains on the surface, resulting in mechanical openings into which the solute or pure liquid can enter and, as a result of adsorption, sets up an internal surface ζ potential, thus making it possible for swelling to proceed further. This conception is substantiated by the fact that the order of swelling of wood in the dry benzene derivatives just given is practically the same as the order of ζ potentials of the same benzene derivatives against cellulose (p. 89) and further a zero ζ potential corresponds to a zero swelling (*230*).

Kistler (*118*) has pointed out the fact that water-swollen gels, including cellulosic materials, will practically retain their completely swollen dimensions when the water is replaced by a completely water-miscible liquid, such as alcohol, which in turn can be replaced by ether or acetone and the latter liquid by a nonpolar liquid, such as a saturated hydrocarbon or benzene.

Kistler (*118*) has prepared aerogels of cellophane using this principle by first carrying the material through the preceding replacement process using propane in the last step because of its low critical temperature. The propane was then removed by heating to 115° C. in an autoclave. The spontaneous vaporization removed all shrinking stress caused by the surface tension at evaporating menisci, thus making it possible to remove the liquid with practically no shrinkage. The aerogel appears white to reflected light and translucent to transmitted light. Upon wetting it becomes transparent and during subsequent drying it shrinks to its original thickness and has the appearance of ordinary cellophane.

Kistler's measurements give no idea as to the amount of the sorbed water that can be removed in this way. The author and Hansen (*232*), however, have recently studied the replacement of water in wood by this general method, determining the residual moisture content as well as the change in external dimensions. It was found that ethylene-glycol monoethyl ether serves admirably as a replacing agent because of its complete miscibility with water and with nonpolar organic liquids. As it boils above the boiling point of water the replacement of the water can be carried out by merely distilling water-swollen specimens in ethylene-glycol monoethyl ether. The residual water remaining in small blocks of wood did not exceed 0.1 to 0.2 percent. When the replacement was carried on sufficiently slowly for the replacing agent to diffuse into the swollen structure as water was distilled off no shrinkage occurred; in fact, the ethylene-glycol monoethyl ether caused a slight swelling beyond the water-swollen dimensions (p. 55) which was partially retained on removal of the water. The replacement of the water-soluble replacing agent by a nonpolar nonswelling organic liquid cannot be carried out so efficiently. A 3-week extraction of the swollen blocks with benzene, in an extractor in which the blocks were kept entirely submerged, removed the ethylene-glycol monoethyl ether within a few tenths of a percent. The shrinkage, however, was equal to about 20 percent of the normal shrinkage from the completely water-swollen to the oven-dry condition. Replacements were made using different replacing media and other nonpolar organic liquids. In all cases a similar shrinkage occurred. Although all of the water held below the fiber-saturation point (29 percent for the white pine used) can be replaced by a water-soluble intermediate replacing agent without accompanying shrinkage, about one-fifth of the replacing agent, corresponding to 5.5-percent moisture content, cannot be replaced by a nonpolar liquid, although it can be removed in the presence of the nonpolar liquid with accompanying shrinkage. It is interesting that this moisture content corresponds closely with the moisture content at the inflection point in the moisture content relative vapor-pressure curves which, in turn, is believed to correspond to the initial surface-bound monomolecular layer of water (*208*, *233*). This surface-bound water can apparently be replaced by swelling agents having an affinity for the wood but it cannot be replaced by nonpolar liquids having no affinity for wood and causing no swelling.

When swollen sections containing these various nonpolar liquids are dried, the normal shrinkage occurs even though these liquids have so little affinity for wood as to cause no swelling of dry wood. The nonpolar liquids must thus be held almost entirely by capillary condensation and the shrinkage must result entirely from capillary forces.

If the intermediate replacing agent is replaced by a nonvolatile molten wax or resin in which it is soluble it is possible to retain, at least partially, the green dimensions of the material. The possibilities of using this as an antishrink treatment for wood has been investigated by the author and Hansen (*232*).

THERMODYNAMICS OF SWELLING

Katz (*92, 110, 111, 114*) has intensively studied the thermodynamics of swelling and has shown that valuable information on the swelling of cellulosic materials can be obtained without regard to structure or swelling mechanism by means of thermodynamic considerations.

It is important to note that thermodynamics predict only real equilibrium conditions. All secondary complications, such as hysteresis, must be excluded. Either data obtained under oscillating humidity conditions or average values of the desorption and adsorption must be used in thermodynamic calculations.

Steinberger (*241*) gives a rather complete summary of the fundamental aspects of the thermodynamics of swelling.

Perhaps the most important conclusion drawn from the first two laws of thermodynamics in regard to swelling is the relationship between swelling pressure and vapor pressure of the swelling medium. If P_s represents the pressure that will just prevent further swelling and $\frac{p}{p_0}$ the relative vapor pressure of the swelling medium in the swelling material, M its molecular weight, v_0 its specific volume, R the gas constant, and T the absolute temperature, then the following equation may be written:

$$P_s = -\frac{RT}{Mv_0} ln \frac{p}{p_0} \qquad (20)$$

With the aid of this equation and moisture content-relative vapor-pressure data the swelling pressures for any moisture content can be calculated. The relationship is of special importance because it is experimentally possible to measure swelling pressures only near the saturation point. No satisfactory measurements have been made of the swelling pressure of cellulosic materials, but Posnjak (*183*) has shown good agreement between the observed and calculated values for gelatin-water and rubber-organic liquid systems. It is well known, however, that at low moisture-content values the swelling pressures of cellulosic materials are tremendous.

Kress and Bialkowsky (*126*) determined the "swelling power" of wood pulp in various liquids; that is, the percentage increase in volume of the pulp caused by imbibition of liquid against a pressure of 3 inches of mercury. They obtained the greatest "swelling power" in formamide, followed by water and various dilute aqueous solutions, and organic liquids in the order of decreasing polarity.

Heats-of-swelling data are of considerable importance in thermodynamic considerations of swelling. Unfortunately, information on the heat of swelling of cellulosic materials is quite meager. Rosenbohm (*192*) has determined the total heat of swelling of several forms of cellulose. Filter paper gave 9.6 calories and cotton 20.8 calories per gram of dry material. Dunlap [12] has measured the total heat of swelling of a number of species of wood at 0° C., obtaining values ranging from 14.6 to 19.6 calories per gram of dry wood. He also determined the heat of wetting of wood by creosote and turpentine, the former giving 4.9 calories and the latter 2.3 calories per gram of dry wood. Measurements of the heat of swelling as a function of the moisture content are still more infrequent. Katz (*110, 111*) gives values for a cellulose and Volbehr (*268*) gives values for a pine wood flour. Katz (*110, 111*) has shown that these data, as well as data on other materials, can be represented by the empirical equation

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[12] DUNLAP, F. HEAT OF ABSORPTION OF WATER IN WOOD. U. S. Dept. Agr. Forest Prod. Lab. Project 169, 10 pp. 1913. (Typewritten report.)

$$H=\frac{ki}{k_1+i} \tag{21}$$

where H is the integral heat of swelling when 1 g of dry substance takes up i g of swelling medium and k and k_1 are constants. Katz (*110, 111*) also gives values for the initial heat of swelling, that is, the differential heat of swelling at zero moisture content $\left(\frac{dH}{di}\right)_{i=0}$. This quantity, which measures the force with which the liquid is bound by the dry material, is high for all swelling materials, amounting to 390 calories for cellulose and 260 calories for wood (*110, 111*) (p. 90).

Argue and Maass (*6*) have recently determined the total heat of swelling of a number of cellulosic materials ranging from 10.2 calories per gram of dry material for standard cotton cellulose to 19.8 calories for the sapwood of an unspecified species (p. 90). They found the heat of swelling of bleached sulphite pulp to increase somewhat on beating. It is questionable on the basis of sorption data if all of the difference is real or if it is partially due to nonattainment of complete equilibrium in the case of the unbeaten and only partially beaten samples. Argue and Maass also determined the differential heat of swelling of the standard cotton cellulose. The normal increase in heat of swelling with decreasing moisture content was obtained. The measurements were not carried above an initial moisture content of 8 percent. A definite hysteresis effect was observed between the measurements made upon samples which were brought to the initial moisture content by desorption and those brought to the initial moisture content by adsorption. The former gave the higher heat of wetting. Initial differential heat of swelling values ranging from 250 to 280 calories per gram of water adsorbed on an infinite amount of cotton were calculated. These values agree with the previous values given for wood (p. 90).

The differential heat of swelling-moisture content relationship can be calculated from moisture content-relative vapor-pressure data at different temperatures, using the integrated form of the Clausius-Clapeyron equation in which the differential heat of swelling

$$\Delta H=\frac{RT_1T_2}{M(T_2-T_1)}\,ln\left(\frac{p_2}{p_1}-\frac{p_0''}{p_0'}\right) \tag{22}$$

p_2 and p_1 being the vapor pressures at temperatures T_2 and T_1, respectively, and p_0'' and p_0' the corresponding saturation pressures. The author and Loughborough have calculated the differential heats of swelling of wood using this equation (*233*). The values agree quite well with the experimental values of Volbehr (*268*) and give an initial heat of swelling of 260 calories per gram of water adsorbed by an infinite amount of wood identical with his value (p. 90). At low moisture-content values the temperature coefficient of ΔH is negligible while at higher values it increases with a decrease in temperature (*233*). They also calculated the initial heat of swelling of cotton using the data of Urquhart and Williams (*257, 262, 263, 264, 265*). A value of 280 calories per gram of water adsorbed on an infinite amount of cotton was obtained (*233*).

An interesting calculation of the internal surface of 1 g of swollen colloidal material a can be made from the total heat of swelling, H, and the adhesion tension A_1, using the following relationship developed by Bartell and Fu (*15*):

$$a=\frac{-H}{A_1-\frac{A_1}{\sigma}T\frac{d\sigma}{dT}} \tag{23}$$

σ being the surface tension of the liquid, and T the absolute temperature. For complete wetting $A_1=\sigma$. The internal surface per gram of cellulosic materials obtained from this relationship varies from 3.5 to 7.5 x 10^6 cm^2, depending upon the heat of swelling (p. 90).

It is also possible to calculate the free energy of swelling from vapor-pressure data. If ΔF is the change in free energy occurring when a large amount of a partially swollen substance within which the vapor pressure of the swelling medium is p takes up one further gram of the medium, then

$$\Delta F=-\frac{RT}{M}ln\frac{p}{p_0} \tag{24}$$

in which the other symbols have the same significance as before.

Considerable insight into the mechanism of swelling can be gained from a comparison of the change of free energy ΔF with the differential heat of swelling ΔH. The difference between these two quantities is thermodynamically equal to the change in entropy ΔS times the absolute temperature,

$$\Delta S=\frac{\Delta H-\Delta F}{T} \tag{25}$$

Earlier measurements by Katz (*110, 111, 114*) showed that the change in free energy and change in heat of swelling are approximately equal, from which he concluded that entropy change was negligible. Recent refined measurements by Fricke and Lüke (*70*) on casein, agar-agar, and keratin, show that the free energy change is in all cases appreciably less than the differential heat of swelling. Calculations made by Loughborough and the author from moisture content-vapor pressure data for wood at different temperatures also showed a similar entropy change that increases from the fiber-saturation point to the dry condition with a slight inflection point at 6- to 8-percent moisture content (*233*).

The entropy calculations of Loughborough and the author (*233*) give surprisingly constant values for the initial entropy change, the entropy change occurring when 1 g of water is added to an infinite amount of dry swelling material for a number of quite different materials. Katz [13] has likewise shown that the initial entropy change of swelling for all materials which he has examined ranges from about 0.3 to 0.35 calories per gram of water adsorbed by an infinite amount of swelling material. This is in excellent agreement with the calculated values of Loughborough and the author. Katz also pointed out that this entropy change is the same as that taking place when water is frozen. It thus appears that the initially adsorbed water, if not in the form of ice, is at least oriented and associated in a similar manner to ice.

ADSORPTION COMPRESSION

When a colloidal material swells in a liquid, the volume of the solid is increased but the total volume solid plus liquid is decreased. X-ray measurements show no sign of a change in the crystal lattice of cellulose on swelling in water, indicating that the volume change is not within the solid. The change is believed to be due to a compression of the adsorbed water caused by an orientation and packing of the water molecules on the surface. This is in keeping with the change in entropy just presented.

With cellulosic materials this effect is quite appreciable. Davidson *(47)* has determined the specific volume of cotton boiled in sodium carbonate and of mercerized cotton as well as regenerated "hydrate" celluloses in toluene, helium, and water. In all cases the values for the helium were just slightly less than the toluene values while the water values were considerably less. For example, a cotton boiled in sodium carbonate gave 0.646 for the specific volume in toluene, 0.642 in helium, and 0.6235 in water. Helium was previously pointed out to be nonadsorbed on cellulosic materials. This fact, combined with the fact that the molecule is small, makes it an ideal material in which to determine the true specific volume. The slightly low values obtained in toluene, a nonswelling liquid, are probably due to incomplete penetration. Other nonswelling liquids give similar values to that obtained with toluene. The large deviation in the opposite direction obtained in water is due to an adsorption compression taking place within the sorbed water. The average specific volume of the adsorbed water in this case is 0.921 and the effective compressive force that would cause it is 2,420 kg per cm^2. It is interesting to note that the apparent specific volumes of "hydrate" celluloses determined in water are less than the specific volumes of the normal celluloses. As their fiber-saturation points are also higher, the compressions instead of being higher are somewhat lower. The regenerated cuprammonium cellulose gives an effective compression of the bound water of 1,890 kg per cm^2.

The author *(221)* has made similar measurements on wood. The apparent specific volume as determined in a series of organic liquids decreases in the increasing order of polarity of the media. This would be expected as the sorption and, consequently, the adsorption compression increase with the polarity of the liquid. The helium values are intermediate between the water and the nonpolar liquid values the same as was found by Davidson for cotton, but they are closer to the water than to the benzene values. It appears in the light of more recent work, however, that the helium values are too low. Measurements of the apparent specific volume of wood were also made in various aqueous solutions. In every case the presence of solute increased the specific volume (*221*). More recent measurements have shown, however, that equilibrium had not been attained, thus giving an apparent osmotic pressure effect. Equilibrium data give identical specific volume values in water and in 2.0 and 20.0 percent solutions of sodium chloride.

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[13] KATZ, J. R. X-RAY SPECTROGRAPHY OF SWELLING. Paper presented at the general session of the Amer. Chem. Soc., Cleveland, 1934. (Unpublished. Title in program.)

Katz (*110, 111, 114*) has shown that the change in the compression with the amount of water adsorbed can be expressed by a hyperbolic empirical equation similar to that relating the heat of swelling with the moisture content. The compression in cubic centimeters resulting from the adsorption of i g of moisture per gram of dry swelling substance:

$$C=\frac{ki}{k_1+i} \tag{26}$$

where k and k_1 are constants. The adsorption compression is a measure of the adsorptive force in the same way as the heat of wetting. Katz believes that the ratio of these two quantities should be constant for different moisture-content values. He has found this to be only approximately so with the data analyzed. He has also compared the initital heat of wetting and the initial compression, both of which are measures of the attractive force of the dry materials for water. For all swelling solids studied, as well as for sulphuric and phosphoric acid mixed with water, the ratio $\frac{C}{H}$ for $i=0$ varied between 1×10^{-3} and 3×10^{-3}. The only cellulosic material for which he gives a value is wood with a ratio of 2.1×10^{-3}.

Filby and Maass (*65*) have recently measured the adsorption compression resulting from the swelling of cotton at different moisture-content values by an ingenious helium displacement method. Their measurements indicate that compression takes place only in the first 8 percent of moisture adsorption and that the compression is constant below 3.5- to 4-percent moisture content. From the former they conclude that only a small part of the sorption is true adsorption and that the remainder is due to capillary condensation. From the latter observation they conclude that 3.5- to 4-percent moisture content corresponds to a monomolecular layer because smaller amounts of moisture are not adsorbed with any greater force. These data are not in harmony with moisture content-relative vapor-pressure data or with heats-of-swelling data (*233*). Vapor-pressure depressions and heats of swelling are obtained at all moisture-content values up to the fiber-saturation point. The compression values which Filby and Maass obtained further seem exceedingly high; for example, the initial sorption corresponds to a calculated compressive force of 100,000 atmospheres, which is about 7.5 times the cohesive force of water. Bartell and Osterhof (*17*) and Bartell and Jennings (*16*) in their adhesion tension measurements have shown that the work of adhesion for a solid wetted by water is but 1.00 to 1.05 times the work of cohesion of water. There is no obvious reason why the same should not be true for cellulose.

The author and Seborg (*234*) have attempted to verify these findings, using a simpler means of measurement. As was shown by the data of Davidson (*47*) the specific volumes of cellulosic materials determined in nonpolar, nonswelling liquids are but slightly greater than the presumably true values determined in helium. Measurements of the compression on the basis of benzene displacement giving the true density of the cellulosic material were hence made pycnometrically in benzene, using the equation:

$$C=\frac{\frac{i}{\rho_a}-\frac{W_b-(W-g-i)}{\rho_b}-\frac{g}{\rho_s}}{g} \tag{27}$$

in which C is the compression in cubic centimeter per gram of swelling material occurring when i g of swelling medium are taken up by g g of swelling material; ρ_a, ρ_b and ρ_s are the densities of water, benzene, and cellulosic substance, respectively; W_b is the weight of the pycnometer filled with the medium to be displaced, and W is the weight of the pycnometer filled with cellulosic material, swelling medium, and medium to be displaced. This method gave true compression values at the higher moisture-content values. At the lower moisture-content values a more accurate value of the true density of the cellulosic substance is required in order to determine the order of magnitude of the compression. A variation of 1.4 percent in the value used for the density of the cellulosic substance, which is approximately the difference in Davidson's density values obtained in helium and in toluene, shifted the initial differential compression per gram of water adsorbed on an infinite amount of cellulosic material from 0.1 to 0.5. This corresponds to a shift in external compressive force sufficient to cause the volume change of 3,400 to 100,000 atmospheres. Further work will thus have to be done to determine this compressive force. Data for the compression taking place in sulphuric acid-water mixtures, which can be obtained with considerable accuracy without any possibility of incomplete penetration causing uncertainties, indicate that the compression is probably of the lower order of magnitude (*234*). Further, the linear moisture content-external shrinkage relationship of wood and the fact that volumetric swelling of wood substance approaches the volume of water taken up (p. 53) are both irreconcilable with high compressions. The confirmation of the finding of Filby and Maass that the compression is constant below a certain moisture content will also require more accurate measurements of the true density of cellulosic substances. The compression measurements in benzene, however, definitely show that compression extends to the fiber-saturation point.

Campbell[14] is of the opinion that the observed compression effects may be entirely fictitious. He favors the conception that water displacement gives the correct specific volume of cellulose and that both helium and nonpolar liquids fail to penetrate the interstices completely because they do not swell the material and hence are not accessible to any internal void structure. Further experimental work will be necessary before this point can be definitely proved. Both Campbell and the author are making measurements upon cellulosic materials in various media that have been retained in a swollen condition by the method of replacement (p. 58). These data should help in determining the existence and magnitude of this highly fundamental property which has been attributed to cellulosic as well as to all other solid materials with a large surface area.

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[14] CAMPBELL, W. B. EFFECT OF WATER ON DENSITY OF CELLULOSE. Quart. Rev. Pulp and Paper Lab., Forest Prod. Lab. Canada 19 (July-Sept. 1934): 8-10. 1934. [Mimeographed.]

SUMMARY

No attempt has been made in this publication to review all the researches dealing with the colloidal properties of cellulosic materials for that would have been an endless task. The bibliography is hence far from complete. The author has attempted more to tie together salient findings regarding the more important colloidal properties of the cellulosic materials. This is difficult in a science that has been more or less an accumulation of isolated facts. It is hoped, however, that this review will stimulate further correlation. The colloid chemistry of cellulosic materials is now at the stage of transition from a qualitative to a quantitative science. Further researches directed towards the determination of the quantitative interrelationship of the various colloidal properties will make possible a more intimate understanding of the physical nature of cellulose which, in turn, will undoubtedly strengthen its claim to being the world's most important organic raw material.

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APPENDIX

SYMBOLS AND EQUATIONS

SYMBOLS

A_1 = adhesion tension in dynes per centimeter.
A = angstrom unit, 10^{-8} centimeter.
a = total surface per gram of material in square centimeters.
b = tensile strength for unit solid fraction in consistent units.
C = compression in cubic centimeters occurring when i g of swelling medium are adsorbed by 1 g of swelling material.
c = concentration of solute in percentage by weight.
D = diffusion constant.
d = derivative sign.
E = drop in electromotive force across membrane or tube in volts.
ΔF = free energy change in gram calories occurring when 1 g of swelling medium is adsorbed by an infinite amount of swelling material.
f = solid fraction of fiber sheet.
f_s = fiber-saturation point in cubic centimeters of water held by 100 g of dry wood.
g = weight of dry swelling material in grams.
H = integral heat of swelling in gram calories evolved when 1 g of dry swelling material takes up i g of swelling medium.
ΔH = differential heat of swelling in gram calories evolved when 1 g of swelling medium is added to an infinite amount of swelling material.
h = height of capillary rise in centimeters.
i = grams of water adsorbed per gram of dry adsorbent.
K = dielectric constant.
k = constant.
L = molecular chain length in angstroms.
l = effective capillary length in centimeters.
l_0 = length of standard capillary in centimeters.
ln = natural logarithm.
M = molecular weight.
m = exponential constant.
$\mathrm{m}\mu$ = 10^{-7} centimeters.
N = Avagadro's number (6.06×10^{23}, number of molecules per gram molecule).
n = number of capillaries in parallel over effective membrane area.
n_γ = axial index of refraction.
n_α = transverse index of refraction.
n_1 and n_2 = index of refraction of components.
P = pressure drop through membrane in dynes.
P_0 = pressure drop through standard capillary in dynes.
P_s = pressure required to just prevent further swelling in dynes.
p = vapor pressure in equilibrium with the capillary system.
p_0 = vapor pressure over a plane surface.
Q = pressure required to overcome the surface tension in dynes.
q = effective capillary cross section in square centimeters.
R = gas constant (8.316×10^7 dynes per square centimeter $\times$ centimeter^3, for other than thermodynamic equations and 1.988-g calories for thermodynamic equations).
r = capillary radius in centimeters.
r_0 = capillary radius of standard capillary in centimeters.
r_p = radius of the particle in centimeters.
ΔS = entropy change.
S_e = volumetric shrinkage transmitted to the external dimensions in percent.
s = specific sedimentation velocity.
T = absolute temperature.
t = time in seconds.
V = velocity of flow in cubic centimeters per second.
V_f = volume of fiber cavities.
v = partial specific volume of sedimenting material.
v_0 = partial specific volume of swelling medium.
W = weight of pycnometer filled with swelling material, adsorbed water, and displacing medium in grams.
W_b = weight of pycnometer filled with displacing medium in grams.

x_1=distance from center of rotation in sedimentation equilibrium system to position in cell where the concentration is c_1 in centimeters.
Z=consistence of pulp stock.
δ=relative volume.
ζ=electrokinetic potential difference set up between the layer of adsorbed ions and the bulk of the solution.
η=viscosity of liquid or solvent in poises.
η_c=viscosity of solution of concentration c in poises.
η_{sp}=increase in relative viscosity caused by solute.
θ=axis ratio of micelles.
κ=specific electrical conductivity of the liquid in the capillary structure in mho.
$\mu=10^{-4}$ centimeters.
ν=extension of the fibers.
$\pi=3.1416$.
ρ=density of liquid or solvent in grams per cubic centimeter.
ρ_a=density of water in grams per cubic centimeter.
ρ_b=density of displacing medium in grams per cubic centimeter.
ρ_s=density of cellulosic substance in grams per cubic centimeter.
ρ_w=bulk density of wood in grams per cubic centimeter on a dry weight-green volume basis.
σ=surface tension in dynes per centimeter.
τ=tensile strength in consistent units.
ϕ=partial specific volume of solute.
ω=angular velocity of centrifuge.

EQUATIONS

No.	Page	Relating	Equation
1	5	Double refraction-components (Wiener).	$n_\gamma^2-n_\alpha^2=\frac{\delta_1\delta_2(n_1^2-n_2^2)^2}{\delta_1n_2^2+\delta_2n_1^2+n_2^2}$
2	16	Overcoming surface tension	$r=\frac{2\sigma}{Q}$
3	17	Flow of liquids through capillaries (Poiseuille).	$V=\frac{n\pi r^4P}{8\eta l}$
4	17	Capillary volume-effective capillary cross section (Dumanski).	$q=1-(1-V_f)^{2/3}=1-\left(1-\frac{\rho_w}{\rho_s}\right)^{2/3}$
5	18	Capillary radius from pressure drop ratio.	$r=\sqrt{\pi\frac{r_o^4lP_o}{l_oqP}}$
6	20	Vapor pressure over a curved surface (Kelvin).	$r=\frac{2\sigma M}{\rho RTlnp_o/p}$
7	22	Rate of capillary rise	$h^2=\frac{r\sigma t}{2\eta}$
8	23	Strength-extensibility of fibers	$\tau=\tau_o\frac{\nu^3}{1-\theta+\theta\nu^3}$
9	24	Strength-solid fraction of sheets.	$\tau=bf^m$
10	24	Strength-consistence of sheets	$b=kZ^{-m'}$
11	24	Strength-solid fraction-consistence of sheets.	$\tau=kf^mZ^{-m'}$
12	28	Diffusion-particle size (Einstein).	$D=\frac{RT}{N}\times\frac{1}{6\eta\pi r_p}$
13	29	Molecular weight-sedimentation velocity (Svedberg).	$M=\frac{RTs}{D(1-v\rho)}$
14	30	Molecular weight-sedimentation equilibrium (Svedberg).	$M=\frac{2RTln(c_2/c_1)}{(1-v\rho)\omega^2(x_2^2-x_1^2)}$
15	30	Viscosity-concentration (Einstein).	$\eta_c=\eta(1+2.5\phi)$
16	30	do	$\eta_{sp}=2.5\phi$

EQUATIONS—continued

No.	Page	Relating	Equation
17	31	Viscosity-molecular weight and molecular chain length (Staudinger).	$\eta_{sp}=k_m cM=k_l cL$
18	34	Electrokinetic potential (Helmholtz).	$\zeta=(300)^2\frac{4\pi\eta\kappa E}{PK}=(300)^2\frac{4\pi\eta V}{EKq}$
19	52	Shrinkage-fiber saturation	$S_e=\rho_w f_s$
20	60	Swelling pressure	$P_s=-\frac{RT}{Mv_0}ln\frac{p}{p_0}$
21	61	Integral heat of swelling-moisture content.	$H=\frac{ki}{k_1+i}$
22	61	Differential heat of swelling-vapor pressure-temperature (Clausius-Clapeyron).	$\Delta H=\frac{RT_1T_2}{M(T_2-T_1)}ln\left(\frac{p_2}{p_1}-\frac{p_0''}{p_0'}\right)$
23	62	Internal surface-heat of swelling-adhesion tension (Bartell-Fu).	$a=\frac{-H}{A_1-\frac{A_1}{\sigma}T\frac{d\sigma}{dT}}$
24	62	Free energy-relative vapor pressure.	$\Delta F=-\frac{RT}{M}ln\frac{p}{p_0}$
25	62	Entropy-energy	$\Delta S=\frac{\Delta H-\Delta F}{T}$
26	64	Compression-moisture content.	$C=\frac{ki}{k_1+i}$
27	65	do	$C=\frac{\frac{i}{\rho_a}-\frac{W_b-(W-g-i)}{\rho_b}-\frac{g}{\rho_s}}{g}$

NUMERICAL DATA

Since many of the properties of cellulosic materials are dependent upon the purity of the cellulose, the physical form of the material, and its previous history, numerical data that have any general significance are difficult to obtain. It is thus possible to give only orders of magnitude for many properties. When ranges of values are given they do not designate the absolute extremes but the range usually obtained.

TABLE 1.—*Refractive indexes and double refractions of cellulose fibers*[1]

Cellulosic material	Axial refractive index n_γ	Transverse refractive index n_α	Double refraction $n_\gamma - n_\alpha$	Calculated angle of inclination of micelles to fiber axis from n_γ	Extensibility		Literature cited
					Calculated	Observed	
				Degrees	*Percent*	*Percent*	
Ramie	1. 595	1. 534	0. 061	0			(*69*).
Do	1. 596	1. 528	. 068	0			(*184*).
Ramie (chlorinated and extracted).	1. 596	1. 525	. 071	0			(*107*).
Flax	1. 594	1. 532	. 062	0			(*69*).
Do	1. 596	1. 528	. 068	0			(*184*).
Flax (chlorinated and extracted).	1. 596	1. 525	. 071	0			(*107*).
Ramie and flax (theoretically pure).	1. 602	1. 526	. 076	0			(*107*).
Nessel	1. 595	1. 533	. 062	0			(*69*).
Cotton	1. 580	1. 534	. 046	30			(*69*).
Do	1. 578	1. 532	. 046	30			(*184*).
Cotton (Farr elliptical particles).	1. 565	1. 530	. 035				(*62*).
Lilienfeld viscose rayon	1. 559	1. 515	. 044	30	11. 5	6. 6	(*184*).
Cuprammonium rayon I	1. 553	1. 518	. 035	33. 2	16. 5	16. 9	
Cuprammonium rayon II	1. 549	1. 520	. 029	39. 2	22. 5	25. 5	
Viscose rayon I	1. 540	1. 519	. 021	47. 9	33. 5	27. 2	
Viscose rayon II	1. 539	1. 519	. 020	50. 8	35. 0	32. 9	
Viscose rayon III	1. 534	1. 518	. 016	54. 7	41. 0	39. 0	

[1] See pp. 5, 6.

TABLE 2.—*Fiber contraction from condition of mercerization under tension to mercerization without tension obtained from the axial index of refractions according to Preston (184)*[1]

Cellulosic material	Mercerization under tension		Mercerization without tension		Contraction	
	Axial refraction n_γ	Angle of inclination θ_0	Axial refraction n_γ	Angle of inclination θ_1	Calculated 100 ($\cos\theta_0 - \cos\theta_1$)	Observed
		Degrees		*Degrees*	*Percent*	*Percent*
Ramie	1. 571	0	1. 556	34. 1	17. 2	21
Flax	1. 571	0	1. 556	34. 1	17. 2	21
Cotton	1. 566	20. 5	1. 554	35. 6	12. 4	14
Lilienfeld viscose rayon	1. 559	28. 8	1. 550	37. 8	9. 8	10

[1] See p. 6.

TABLE 3.—*Dimensions of unit cell of cellulose obtained from X-ray crystal lattice measurements of cellulose from different sources*[1]

Crystal form	Glucose units in unit cell (munber)	Dimensions of unit cell				Literature citation
		a	*b*	*c*	*β*	
Monoclinic	4	8.3A	10.3A	7.9A	84°	(*152*)

[1] See p. 7.

TABLE 4.—*Time for complete development of cellulose fibers* [1]

Kind	Days	Literature citation
	Number	
Wood	10	*(191)*
Cotton	50	*(40)*

[1] See pp. 7, 8.

TABLE 5.—*Size of structural units of wood* [1]

Structure	Average dimension		Means of measurement	Literature citation	Remarks
	Length	Breadth			
Fibers:	*Cm.*	*Cm.*			
Softwoods	3×10^{-1}	3×10^{-3}	Microscopic	*(189)*	Wall thickness 0.1 to 0.3 of fiber breadth.
Hardwoods	1×10^{-1}	1×10^{-3}	do	*(190)*	
Sleeves	1×10^{-1}		do		5 to 10 concentric sleeves to fiber.
Fibrils	1×10^{-1}	3×10^{-4}	do		
Fusiform bodies	5×10^{-4}	1×10^{-4}	do		
Spherical units		2×10^{-5}	do		
Micelles	5×10^{-6}	5×10^{-7}	Spreading of X-ray diffraction rings.	*(87)*	Cellulose constituent only.
Unit cell	1×10^{-7}	8×10^{-8}	X-ray	*(152)*	Do.

[1] See pp. 10, 11.

TABLE 6.—*Pore radii of membranes* [1]

Measurement	Material	Pore radius (millimicrons)	Literature cited
Most effective pore radius	Cellophane	20–30	*(141)*
	Collodion films	300–800	*(14)*
	do	90–250	*(20)*
	Softwoods (pit membranes):		
	Heartwood	40–5,000	*(220, 227, 230)*
	Sapwood	180–11,000	
Average effective pore radius	Cellulose acetate	13	*(52)*
	Viscose films	1.5	*(157)*
	Viscose swollen in sodium hydroxide	9.4	*(157)*
	Collodion films	3–20	*(99)*
	do	0.9–30	*(26)*
	do	55	*(20)*
	Softswoods (pit membranes):		
	Heartwood	7–36	*(220, 230)*
Average effective capillary radius in sheet direction.	Blotting and cartridge papers	20–1,000	*(212)*
	Filter paper	4,000–40,000	*(176)*

[1] See pp. 16–22.

TABLE 7.—*Tensile strength of various fibers* [1]

Material	Tensile strength	Literature citation
	Kg per sq. mm	
Flax	100	*(143)*
Cotton	[2] 28	
Wood	8–15	
Ordinary viscose	25	
Well-oriented viscose	80	
Paper	0. 5–8. 0	*(49)*
Paper (unit solid fraction and maximum orientation)	30	
Cellulose (theoretical ultimate strength of primary valence chain)	800	*(143)*

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[1] See p. 23.

[2] The Bureau of Agricultural Economics report values ranging from 40 to 70 kg per mm^2 for the tensile strength of cotton.

TABLE 8.—*Particle size, molecular weight, and molecular dimensions of cellulose determined by eight methods* [1]

Material	State	Method	Molecular weight	Molecular chain length	Molecular cross-sectional diameter	Remarks	Literature citation
				A	*A*		
Ramie fibers	Solid	X-ray	1,000,000	500	50		(*87*)
Cotton	In cuprammonium solvent.	Diffusion	500,000		100	Assumed spherical.	(*90*)
Cotton linters alpha cellulose.	do	Sedimentation velocity.	40,000			Cu free basis	(*223*)
Do	do	Sedimentation equilibrium.	42,000			do	(*223*)
Do	do	do	200,000–300,000			Including Cu	(*124*)
Cotton (Farr particles).	do	do	50,000				([2])
Cellulose derivatives.	Organic solvents.	do	100,000–200,000			Including Cu	(*124*)
Cotton	In cuprammonium solvent.	Viscosity	120,000	3,900			(*237*)
Do	In phosphoric acid.	do	340,000			Calculated for zero time in solution.	(*58*)
Methyl cellulose.		Analytical	20,000–40,000	500–1,000		Assumed single chains.	(*83*)
Cellulose derivatives.	Organic solvents.	Osmotic pressure.	18,000–50,000				(*54*)
Do	do	do	35,000–45,000				(*33*)
Do	On water and on mercury.	Spreading			3–8		(*1, 117, 205*)

[1] See pp. 28–32.
[2] Kraemer (unpublished).

TABLE 9.—*Electrical conductivity* [1]

Item	Material	Units	Literature citation
Specific electrical conductivity at about 25° C	Dry wood	10^{-18} mgo	(*41*)
Increase in moisture content required to double electrical conductivity.	Wood	1.5 percent	(*219*)
	Cotton	1.2 percent	(*268*)
Increase in surface conductivity over bulk conductivity (solid-distilled water system).	Cellulose	10 times	(*28*)

[1] See p. 33.

TABLE 10.—*ζ potential of cellulosic materials against distilled water in volts* [1]

Material	Volts	Literature citation
Cotton	0.0157	(*76, 78*)
Do	.0290	(*105*)
Cotton, beaten 216 hours	.0451	
Filter paper	0.0161–.0214	(*29*)
Sulphite pulp	.0083	(*29*)
Do	.0119	(*105*)
Sulphite pulp, beaten 216 hours	.0182	(*105*)
Wood	.014	(*215, 220*)

[1] See pp. 34, 35.

TABLE 11.—*Sorption of gases by cellulosic materials in cubic centimeters per gram of dry adsorbent* [1]

Material	Gas	Sorption	Literature citation
Cotton	Air	0.023	*(47)*
Wood	H_2	.013	*(221)*
Do	N_2	.020	
Do	O_2	.042	

[1] See p. 39.

TABLE 12.—*Adsorption of polar gases and vapors by cellulosic materials* [1]

Material	Gas or vapor	Temperature	Pressure	Relative vapor pressure	Sorption weight	Literature citation
		°C.	*Centimeter of mercury*	*Percent*	*Percent*	
Cotton	Hydrochloric acid	22	5.4		0.8	*(73)*
Do	do	22	70.2		2.0	
Wood (white spruce)	do	22	5.0		3.2	
Do	do	22	75.0		10.5	
Cotton	Sulphur dioxide	22	76.0		5.0	
Wood	do	22	76.0		13.6	
Cotton	Ammonia	22	76.0		4.0	
Wood	do	22	76.0		7.4	
Do	Carbon dioxide	22	42.0		1.0	
Do	do	22	76.0		1.0	
Do	Amylene	22	25.0		.5	
Do	do	22	76.0		.5	
Do	Ether	22	10.2		.5	
Do	do	22	38.2		1.2	
Do	Methyl alcohol	22		34.4	6.4	
Do	do	22		83.1	11.7	
Ground wood	do	20		11.0	6.9	*(37)*
Do	do	20		39.7	11.1	
Do	do	20		100.0	27.5	
Bleached sulphite pulp	do	20		11.0	3.8	
Do	do	20		39.7	6.9	
Do	do	20		100.0	19.3	
Cotton	do	30		100.0	11.2	*(207)*
Do	Ethyl alcohol	30		100.0	8.6	
Do	Propyl alcohol	30		100.0	5.0	
Do	N-butyl alcohol	30		100.0	1.5	

[1] See pp. 39, 50.

TABLE 13.—*Sorption of water vapor at saturation by cellulosic materials*[1]

Material	Temperature[2]	Sorption weight	Literature citation
	°*C*	*Percent*	
Standard cotton	30	17.51	(*204, 206*)
Do	20	16.8	(*169*)
Do	30	15.2	(*169*)
Cotton linters	30	14.97	(*204, 206*)
Cotton, boiled in sodium carbonate	25	23.76	(*257, 262, 263, 264, 265*)
Cotton, mercerized	25	39.23	
Cotton linters, mercerized	30	22.69	(*204, 206*)
"Hydrate" cellulose:			
Regenerated from cuprammonium solution	30	23.47	
Hydrolyzed from cellulose acetate	30	26.57	
Viscose rayons	25	33–45	(*261*)
Cellophane	25	33	
Lilienfeld viscose rayon	25	35–39	
Cuprammonium rayons	25	35–41	
Oxycellulose	30	11.89	(*204, 206*)
Hydrocellulose	30	10.39	
Alpha cellulose pulp	20	23.3	(*169*)
Do	30	18.0	
Alpha cellulose, bamboo	20	26.0	
Do	30	25.8	
Unbleached sulphite pulp, beaten and unbeaten	25	25–30	(*37*)
Do	25	28	(*201*)
Kraft pulp, beaten and unbeaten	25	30	(*37*)
Cellulose acetate rayon	25	18	(*261*)
Cellulose nitrate	20	6.7	(*169*)
Wood	25	26–31	(*155*)
Do	23	21–31	(*73*)
Do	25	24–31	(*180*)
Do	25	27–31	(*219, 229, 233*)
Tree barks	25	22–30	(*111*)

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[1] See p. 48.

[2] Effect of temperature: Cotton −10° to +50° C., approximately 0.1 percent increase per degree centigrade decrease (*257, 262, 263, 264, 265*); wood 20 to 100°, approximately 0.1 percent increase per degree centigrade decrease (*233*).

TABLE 14.—*Properties of activated or hydrated cellulose versus the properties of degraded or hydro and oxy celluloses*[1]

Material	Treatment	Tensile strength (dynes/cm² × 10⁻⁹)	Relative fluidity in 0.5-percent cuprammonium solution	Braidy copper no. (gram of Cu reduced by 100 g of cellulose)	Relative absorption of methylene blue	Relative sorption of H_2O at 50-percent relative vapor pressure	Relative absorption of NaOH from N/2 solution	Relative sorption of $Ba(OH)_2$ from N/5 solution
Natural cotton	Dilute NaOH	4.9	1.0	0.02	1.0	1.0	1.0	1.0
Degraded cotton:								
Hydro-cellulose	HCl	1.5	23.0	2.44	--------	.97	(2)	(2)
Oxy-cellulose	NaBrO	2.4	20.7	.5	3.7–10.0	.97	(2)	(2)
	HClO	--------	19.4	3.4	1.4– 3.7	--------	(2)	(2)
Activated cotton	Concentrated NaOH, no tension.	(3)	(3)	(3)	(3)	1.50	2.55	2.70
	Concentrated NaOH, tension.	(3)	(3)	(3)	(3)	1.35	1.96	2.05
	Concentrated NaOH, dried under tension at 110° C.	(3)	(3)	(3)	(3)	1.20	1.89	1.99
	Concentrated H_2SO^4, no tension.	(3)	(3)	(3)	(3)	1.83	3.20	3.20
Cellulose both degraded and activated.	Viscose rayon	4.0	40.0	1.1	--------	1.8–2.0	3.4–3.6	3.8–4.0
	Cuprammonium rayon.	--------	28.0	.5	--------	--------	--------	--------

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[1] Data assembled by Neale (*164*), see p. 44.

[2] Unaffected by degradation.

[3] Unaffected by activation.

Table 15.—*Fiber-saturation point in percentage of oven-dry weight of unbleached spruce sulphite pulp and spruce wood at about 25° C. obtained by 6 methods* [1]

Method	Material	Fiber-saturation point	Literature citation
		Percent	
Moisture content-relative vapor pressure	Unbleached spruce sulphite pulp	28.0	(*201*)
	Spruce wood	31.0	(*219, 233*)
	do	28.0	(*155*)
Electrical conductivity	Unbleached spruce sulphite pulp	27.0	(*201*)
	Spruce wood	29.0	(*219*)
Shrinkage:			
Volumetric	do	28.0	(*155*)
Do	do	28.5	(*218, 229*)
Tangential	do	30.0	(*219*)
Do	do	28.0	(*155*)
Radial	do	28.0	(*219*)
Do	do	28.0	(*155*)
Strength:			
Modulus of rupture	do	27.0	(*251, 279*)
Stress at elastic limit in bending	do	25.0	(*251, 279*)
Maximum crushing strength parallel to grain.	do	27.0	(*251, 279*)
Proportional limit stress compression perpendicular to the grain.	do	27.0	(*251, 279*)
Heat of wetting	do	29.0	(*233*)
Adsorption compression	Unbleached spruce sulphite pulp	27.5	(*234*)
	Spruce wood	29.0	(*234*)

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[1] See p. 47.

Table 16.—*External volumetric swelling of small sections of white pine in various liquids from the oven-dry condition (232)* [1]

Swelling media	External volumetric swelling	Dipole moment ($\times 10^{18}$)	ζ potential of cellulose (*148*)
	Percent		*Millivolts*
Benzene	0	0	0
Toluene	.17	.4	−.2
Chlorbenzene	.54	1.52	−1.0
Brombenzene	.60	1.50	−6.7
Aniline	.50	1.56	−49.7
Benzaldehyde	.62	2.75	
Nitrobenzene	1.42	3.90	−142.0
Formic acid	12.56		
Acetic acid	7.85		
Propionic acid	6.96		
Valeric acid	5.90		
Oleic acid	4.08		
Water	10.34		
Methyl alcohol	9.87		
Ethyl alcohol	8.65		
Propyl alcohol	4.65		
N-butyl alcohol	1.40		
Amyl alcohol	.51		

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[1] See p. 58.

TABLE 17.—*Inner surface of sorption of cellulosic materials* [1]

Available for—	Method	Surface	Literature citation
		Sq. cm per g	
Sorption of water and other swelling agents.	From adsorption compression and assumption that attractive force varies as fifth power of distance for wood.	3×10^{5}	(*221*).
	From adsorption of sulphur dioxide on native cotton.	1×10^{7}	(*208*).
	From adsorption limits of cellulose acetate.	6×10^{6}	(*208*).
	From heats of wetting and adhesion tension:		
	For wood	$6\text{–}7\times10^{6}$	(Table 18 and equation 23).
	For cellulose	$3.5\text{–}7.5\times10^{6}$	
Sorption of nonswelling agents on the dry material.	Estimate from microscopic measurements for wood.	$1\text{–}5\times10^{3}$	

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[1] See p. 62.

TABLE 18.—*Total heat of swelling of cellulosic materials in water in calories per gram of dry material* [1]

Material	Heat of swelling	Literature citation
Filter paper	9.6	(*192*).
Cotton	20.8	(*192*).
Standard cotton	10.16	(*6*).
Cotton pulp	10.54	
Kraft pulp	13.08	
Bleached sulphite pulp—Beating time:		
0 minutes	12.68	
10 minutes	13.01	
20 minutes	13.48	
30 minutes	13.61	
40 minutes	13.92	
Wood meal:		
Sapwood:		
Passes 100 mesh	19.78	
Passes 40 but not 100 mesh	19.26	
Heartwood:		
Passes 100 mesh	18.41	
Passes 40 but not 100 mesh	18.13	
Wood	14.6–19.6	(See p. 61.)
Pine	17.0	(*268*).

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[1] See p. 61.

TABLE 19.—*Initial differential heat of swelling of cellulosic materials in water in calories per gram of water adsorbed by an infinite amount of cellulosic material* [1]

Material	Heat of swelling	Literature citation
Cotton	390	(*110, 111*).
Do	250–280	(*6*).
Cotton (calculated from vapor pressure-moisture content-temperature relationship, using data of Urquhart and Williams)	280	(*233*).
Wood:		
Pine	260	(*110, 111, 268*).
Spruce (calculated from vapor pressure-moisture content-temperature relationship)	260	(*233*).

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[1] See p. 61.

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